

Physical Methods in Chemistry and Nano Science

Collection Editor:

Andrew R. Barron

Physical Methods in Chemistry and Nano Science

Collection Editor:

Andrew R. Barron

Authors:

John J. Allen	Meghan Jebb
Andrew R. Barron	Chengmin Jiang
Simon Bott	Wilhelm Kienast
Cara Bovet	Sequoyah King
Jarrold Boyd	Inna Kurganskaya
Ariana Bratt	Michelle LaComb
Pinn-Tsong Chiang	Justin Law
Brandon Cisneros	Jiebo Li
Charles Conn	Lei Li
Laurie Cullum	Xianyu Li
Paul Derry	Wayne Lin
Gabriela Escalera	Yen-Hao Lin
Huiling Fei	Yen-Tien Lu
Ezekial Fisher	Andreas Luttge
Dennis J. Flood	Samuel Maguire-Boyle
Varun Shenoy Gangoli	Danielle Michaud
Ayrat Gizzatov	Shawdon Molavi
Natalia Gonzalez Pech	Gabriel Oaxaca
Amanda M. Goodman	Brittany L. Oliva
Sravani Gullapalli	Alvin Orbaek
Ty Hanna	Sehmus Ozden
Lauren Harrison	Courtney Payne
Mayra Hernandez Rivera	Zhiwei Peng
Kewei Huang	Graham Piburn
Chih-Chau Hwang	Stacy Prukop
Nina Hwang	Tawana Robinson

Gedeng Ruan
Hannah Rutledge
Avishek Saha
Richa Sethi
Basil Shadfan
Carissa Smith
Nikolaos Soultanidis
Zhengzong Sun
Ryan Thaner

Juan Velazquez
Farrukh Vohidov
Xiewen Wen
Changsheng Xiang
Zheng Yan
Ruquan Ye
Zhun Zhao
Caoimhe de Fréin

Online:

< <http://cnx.org/content/col10699/1.14/> >

C O N N E X I O N S

Rice University, Houston, Texas

This selection and arrangement of content as a collection is copyrighted by Andrew R. Barron. It is licensed under the Creative Commons Attribution 3.0 license (<http://creativecommons.org/licenses/by/3.0/>).

Collection structure revised: June 26, 2012

PDF generated: June 26, 2012

For copyright and attribution information for the modules contained in this collection, see p. 681.

Table of Contents

Introduction	1
1 Elemental Analysis	
1.1 Introduction to Atomic Absorption Spectroscopy	3
1.2 ICP-AES Analysis of Nanoparticles	17
1.3 ICP-MS for Trace Metal Analysis	24
1.4 Introduction to Combustion Analysis	28
1.5 Ion Selective Electrode	43
1.6 A Practical Introduction to X-ray Absorption Spectroscopy	47
1.7 Fluorescence Spectroscopy	58
1.8 X-ray Photoelectron Spectroscopy	75
1.9 Auger Electron Spectroscopy	84
1.10 An Introduction to Energy Dispersive X-ray Spectroscopy	90
1.11 Rutherford Backscattering of Thin Films	98
1.12 An Accuracy Assessment of the Refinement of Crystallographic Positional Metal Disorder in Molecular Solid Solutions	106
1.13 Principles of Gamma-ray Spectroscopy and Applications in Nuclear Forensics Solutions	111 117
2 Physical and Thermal Analysis	
2.1 Melting Point Analysis	119
2.2 Solution Molecular Weight of Small Molecules	123
2.3 Molecular Weight of Polymers	129
2.4 Size Exclusion Chromatography and its Application in Polymer Science	144
2.5 Thermogravimetric Analysis	154
2.6 Differential Scanning Calorimetry (DSC)	180
2.7 BET Surface Area Analysis of Nanoparticles	185
2.8 Introduction to Cyclic Voltammetry Measurements	196
2.9 Determination of Relaxation Parameters of Contrast Agents Solutions	206 211
3 Chemical Speciation	
3.1 Magnetism	213
3.2 Raman Spectroscopy	241
3.3 IR Spectroscopy	261
3.4 UV-Visible Spectroscopy	288
3.5 Photoluminescence and Fluorescence Spectroscopy	295
3.6 Mossbauer Spectroscopy	315
3.7 NMR Spectroscopy	321
3.8 EPR Spectroscopy	355
3.9 X-ray Photoelectron Spectroscopy	365
3.10 ESI-QTOF-MS Coupled to HPLC and its Application for Food Safety	380
3.11 Mass Spectrometry Solutions	388 395
4 Reactions Kinetics and Pathways	
4.1 Dynamic Headspace Gas Chromatography Analysis	397
4.2 Gas Chromatography Analysis of the Hydrodechlorination Reaction of Per-chloroethylene	408
4.3 Temperature-Programmed Desorption Mass Spectroscopy Applied in Surface Chemistry	413

5 Dynamic Processes

- 5.1 NMR of Dynamic Systems: An Overview 425
- 5.2 Rolling Molecules on Surfaces Under STM Imaging 429

6 Molecular and Solid State Structure

- 6.1 Crystal Structure 441
- 6.2 Structures of Element and Compound Semiconductors 459
- 6.3 X-ray Crystallography 470
- 6.4 Neutron Diffraction 492
- 6.5 XAFS 502
- 6.6 Circular Dichroism Spectroscopy and its Application for Determination of Secondary Structure of Optically Active Species 509
- 6.7 Protein Analysis using Electrospray Ionization Mass Spectroscopy 518
- 6.8 The Analysis of Liquid Crystal Phases using Polarized Optical Microscopy 526

7 Structure at the Nano Scale

- 7.1 Microparticle Characterization via Confocal Microscopy 535
- 7.2 Transmission Electron Microscopy 542
- 7.3 Scanning Tunneling Microscopy 560
- 7.4 Spectroscopic Characterization of Nanoparticles 577
- 7.5 Measuring the Specific Surface Area of Nanoparticle Suspensions using NMR 608
- 7.6 Characterization of Graphene by Raman Spectroscopy 619

8 Surface Morphology and Structure

- 8.1 The Application of VSI (Vertical Scanning Interferometry) to the Study of Crystal Surface Processes 623
- 8.2 Atomic Force Microscopy 634
- 8.3 SEM and its Applications for Polymer Science 639
- 8.4 Catalyst Characterization Using Thermal Conductivity Detector 650

9 Device Performance

- 9.1 A Simple Test Apparatus to Verify the Photoresponse of Experimental Photovoltaic Materials and Prototype Solar Cells 661

Index	670
Attributions	681

Introduction

Course Introduction

Chem 475 is a survey course of research techniques used in modern chemistry, materials science, and nano science. The topics are grouped, not by method *per se*, but with regard to the type of information that can be obtained. Thus, the topics are ordered as follows:

- Elemental composition.
- Physical and thermal analysis.
- Chemical speciation.
- Dynamic processes.
- Reaction kinetics and pathways.
- Molecular structure.
- Structure at the nano scale.
- Surface morphology and structure.
- Optical properties.
- Device performance.

As a consequence of this organization methods can be found in different chapters. For example, X-ray photoelectron spectroscopy is included under *elemental composition* with regard to its use for determining the chemical composition, while it is included under *chemical speciation* with regard to determining the identity of component chemical moieties.

The modules in this course (to date) have been developed by the students in the class and the topics are representative of their research interests. As the course develops, further modules will be added and consequently some may overlap in subject matter.

¹This content is available online at <<http://cnx.org/content/m23040/1.9/>>.

Chapter 1

Elemental Analysis

1.1 Introduction to Atomic Absorption Spectroscopy ¹

1.1.1 Brief overview of atomic absorption spectroscopy

1.1.1.1 History of atomic absorption spectroscopy

The earliest spectroscopy was first described by Marcus Marci von Kronland in 1648 by analyzing sunlight as is passed through water droplets and thus creating a rainbow. Further analysis of sunlight by William Hyde Wollaston (Figure 1.1) led to the discovery of black lines in the spectrum, which in 1820 Sir David Brewster (Figure 1.2) explained as absorption of light in the sun's atmosphere.



Figure 1.1: English chemist and physicist William Hyde Wollaston (1659 - 1724).

¹This content is available online at <<http://cnx.org/content/m38330/1.1/>>.



Figure 1.2: Scottish physicist, mathematician, astronomer, inventor, writer and university principal Sir David Brewster (1781 - 1868).

Robert Bunsen (Figure 1.3) and Gustav Kirchhoff (Figure 1.4) studied the sodium spectrum and came to the conclusion that every element has its own unique spectrum that can be used to identify elements in the vapor phase. Kirchhoff further explained the phenomenon by stating that if a material can emit radiation of a certain wavelength, that it may also absorb radiation of that wavelength. Although Bunsen and Kirchhoff took a large step in defining the technique of atomic absorption spectroscopy (AAS), it was not widely utilized as an analytical technique except in the field of astronomy due to many practical difficulties.



Figure 1.3: German chemist Robert Bunsen (1811 - 1899).

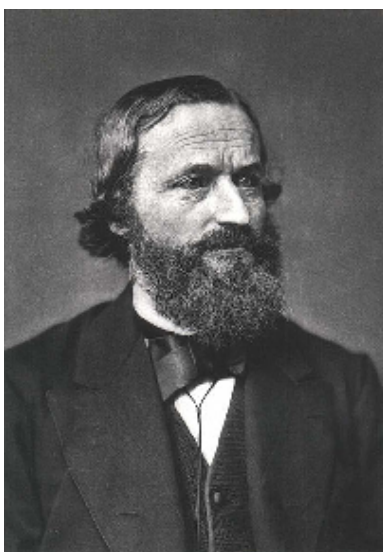


Figure 1.4: German physicist Gustav Robert Kirchhoff (1824 - 1887).

In 1953, Alan Walsh (Figure 1.5) drastically improved the AAS methods. He advocated AAS to many

instrument manufacturers, but to no avail. Although he had improved the methods, he hadn't shown how it could be useful in any applications. In 1957, he discovered uses for AAS that convinced manufacturers market the first commercial AAS spectrometers. Since that time, AAS's popularity has fluctuated as other analytical techniques and improvements to the methods are made.



Figure 1.5: British physicist Sir Alan Walsh (1916 - 1988).

1.1.1.2 Theory of atomic absorption spectroscopy

In order to understand how atomic absorption spectroscopy works, some background information is necessary. Atomic theory began with John Dalton (Figure 1.6) in the 18th century when he proposed the concept of atoms, that all atoms of an element are identical, and that atoms of different elements can combine to form molecules. In 1913, Niels Bohr (Figure 1.7) revolutionized atomic theory by proposing quantum numbers, a positively charged nucleus, and electrons orbiting around the nucleus in the what became known as the *Bohr model of the atom*. Soon afterward, Louis deBroglie (Figure 1.8) proposed quantized energy of electrons, which is an extremely important concept in AAS. Wolfgang Pauli (Figure 1.9) then elaborated on deBroglie's theory by stating that no two electrons can share the same four quantum numbers. These landmark discoveries in atomic theory are necessary in understanding the mechanism of AAS.



Figure 1.6: English chemist, physicist, and meteorologist John Dalton FRS (1766 - 1844).



Figure 1.7: Danish physicist Niels Henrik David Bohr (1885 - 1962).



Figure 1.8: French physicist and a Nobel laureate Louis de Broglie (1892 - 1987). Copyright: American Institute of Physics.



Figure 1.9: Austrian physicist Wolfgang Pauli (1900 - 1958).

Atoms have valence electrons, which are the outermost electrons of the atom. Atoms can be excited when irradiated, which creates an absorption spectrum. When an atom is excited, the valence electron moves up an energy level. The energies of the various stationary states, or restricted orbits, can then be determined

by these emission lines. The resonance line is then defined as the specific radiation absorbed to reach the excited state.

The Maxwell-Boltzmann equation gives the number of electrons in any given orbital. It relates the distribution to the thermal temperature of the system (as opposed to electronic temperature, vibrational temperature, or rotational temperature). Plank proposed radiation emitted energy in discrete packets (quanta) (1.1), which can be related to Einstein's equation, (1.2).

$$E = h\nu \quad (1.1)$$

$$E = mc^2 \quad (1.2)$$

Both atomic emission and atomic absorption spectroscopy can be used to analyze samples. Atomic emission spectroscopy measures the intensity of light emitted by the excited atoms, while atomic absorption spectroscopy measures the light absorbed by atomic absorption. This light is typically in the visible or ultraviolet region of the electromagnetic spectrum. The percentage is then compared to a calibration curve to determine the amount of material in the sample. The energy of the system can be used to find the frequency of the radiation, and thus the wavelength through the combination of equations (1.2) and (1.3).

$$\nu = c/\lambda \quad (1.3)$$

Because the energy levels are quantized, only certain wavelengths are allowed and each atom has a unique spectrum. There are many variables that can affect the system. For example, if the sample is changed in a way that increases the population of atoms, there will be an increase in both emission and absorption and *vice versa*. There are also variables that affect the ratio of excited to unexcited atoms such as an increase in temperature of the vapor.

1.1.2 Applications of atomic absorption spectroscopy

There are many applications of atomic absorption spectroscopy (AAS) due to its specificity. These can be divided into the broad categories of biological analysis, environmental and marine analysis, and geological analysis.

1.1.2.1 Biological analysis

Biological samples can include both human tissue samples and food samples. In human tissue samples, AAS can be used to determine the amount of various levels of metals and other electrolytes, within tissue samples. These tissue samples can be many things including but not limited to blood, bone marrow, urine, hair, and nails. Sample preparation is dependent upon the sample. This is extremely important in that many elements are toxic in certain concentrations in the body, and AAS can analyze what concentrations they are present in. Some examples of trace elements that samples are analyzed for are arsenic, mercury, and lead.

An example of an application of AAS to human tissue is the measurement of the electrolytes sodium and potassium in plasma. This measurement is important because the values can be indicative of various diseases when outside of the normal range. The typical method used for this analysis is atomization of a 1:50 dilution in strontium chloride (SrCl_2) using an air-hydrogen flame. The sodium is detected at its secondary line (330.2 nm) because detection at the first line would require further dilution of the sample due to signal intensity. The reason that strontium chloride is used is because it reduces ionization of the potassium and sodium ions, while eliminating phosphate's and calcium's interference.

In the food industry, AAS provides analysis of vegetables, animal products, and animal feeds. These kinds of analyses are some of the oldest application of AAS. An important consideration that needs to be taken into account in food analysis is sampling. The sample should be an accurate representation of what is being analyzed. Because of this, it must be homogenous, and many it is often needed that several samples are run. Food samples are most often run in order to determine mineral and trace element amounts so that

consumers know if they are consuming an adequate amount. Samples are also analyzed to determine heavy metals which can be detrimental to consumers.

1.1.2.2 Environmental and marine analysis

Environmental and marine analysis typically refers to water analysis of various types. Water analysis includes many things ranging from drinking water to waste water to sea water. Unlike biological samples, the preparation of water samples is governed more by laws than by the sample itself. The analytes that can be measured also vary greatly and can often include lead, copper, nickel, and mercury.

An example of water analysis is an analysis of leaching of lead and zinc from tin-lead solder into water. The solder is what binds the joints of copper pipes. In this particular experiment, soft water, acidic water, and chlorinated water were all analyzed. The sample preparation consisted of exposing the various water samples to copper plates with solder for various intervals of time. The samples were then analyzed for copper and zinc with air-acetylene flame AAS. A deuterium lamp was used. For the samples that had copper levels below 100 $\mu\text{g/L}$, the method was changed to graphite furnace electrothermal AAS due to its higher sensitivity.

1.1.2.3 Geological analysis

Geological analysis encompasses both mineral reserves and environmental research. When prospecting mineral reserves, the method of AAS used needs to be cheap, fast, and versatile because the majority of prospects end up being of no economic use. When studying rocks, preparation can include acid digestions or leaching. If the sample needs to have silicon content analyzed, acid digestion is not a suitable preparation method.

An example is the analysis of lake and river sediment for lead and cadmium. Because this experiment involves a solid sample, more preparation is needed than for the other examples. The sediment was first dried, then grounded into a powder, and then was decomposed in a bomb with nitric acid (HNO_3) and perchloric acid (HClO_4). Standards of lead and cadmium were prepared. Ammonium sulfate ($[\text{NH}_4][\text{SO}_4]$) and ammonium phosphate ($[\text{NH}_4]_3[\text{PO}_4]$) were added to the samples to correct for the interferences caused by sodium and potassium that are present in the sample. The standards and samples were then analyzed with electrothermal AAS.

1.1.3 Instrumentation

1.1.3.1 Atomizer

In order for the sample to be analyzed, it must first be atomized. This is an extremely important step in AAS because it determines the sensitivity of the reading. The most effective atomizers create a large number of homogenous free atoms. There are many types of atomizers, but only two are commonly used: flame and electrothermal atomizers.

1.1.3.1.1 Flame atomizer

Flame atomizers Figure 1.10 are widely used for a multitude of reasons including their simplicity, low cost, and long length of time that they have been utilized. Flame atomizers accept an aerosol from a nebulizer into a flame that has enough energy to both volatilize and atomize the sample (Figure 1.10). When this happens, the sample is dried, vaporized, atomized, and ionized. Within this category of atomizers, there are many subcategories determined by the chemical composition of the flame. The composition of the flame is often determined based on the sample being analyzed. The flame itself should meet several requirements including sufficient energy, a long length, non-turbulent, and safe.

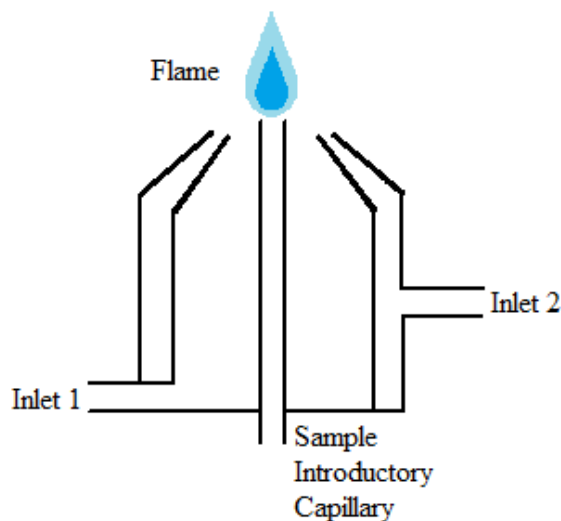


Figure 1.10: A schematic diagram of a flame atomizer showing the oxidizer inlet (1) and fuel inlet (2).

1.1.3.1.2 Electrothermal atomizer

Although electrothermal atomizers were developed before flame atomizers, they did not become popular until more recently due to improvements made to the detection level. They employ graphite tubes that increase temperature in a stepwise manner (Figure 1.11). Electrothermal atomization first dries the sample and evaporates much of the solvent and impurities, then atomizes the sample, and then rises it to an extremely high temperature to clean the graphite tube. Some requirements for this form of atomization are the ability to maintain a constant temperature during atomization, have rapid atomization, hold a large volume of solution, and emit minimal radiation. Electrothermal atomization is much less harsh than the method of flame atomization.

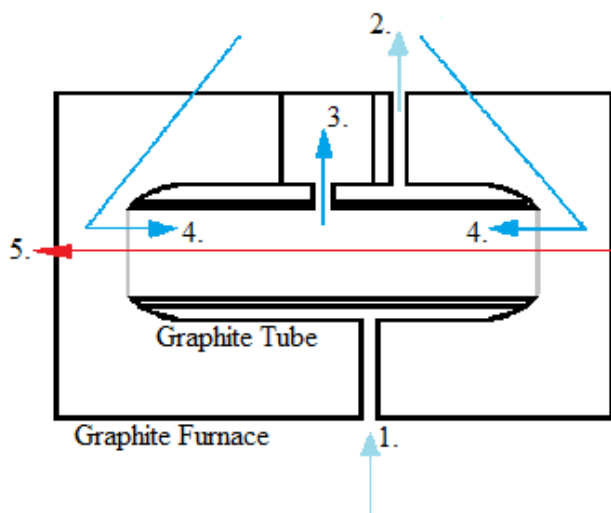


Figure 1.11: Schematic diagram of an electrothermal atomizer showing the external gas flow inlet (1), the external gas flow outlet (2), the internal gas flow outlet (3), the internal gas flow inlet (4), and the light beam (5).

1.1.3.2 Radiation source

The radiation source then irradiates the atomized sample. The sample absorbs some of the radiation, and the rest passes through the spectrometer to a detector. Radiation sources can be separated into two broad categories: line sources and continuum sources. Line sources excite the analyte and thus emit its own line spectrum. Hollow cathode lamps and electrodeless discharge lamps are the most commonly used examples of line sources. On the other hand, continuum sources have radiation that spreads out over a wider range of wavelengths. These sources are typically only used for background correction. Deuterium lamps and halogen lamps are often used for this purpose.

1.1.3.3 Spectrometer

Spectrometers are used to separate the different wavelengths of light before they pass to the detector. The spectrometer used in AAS can be either single-beam or double-beam. Single-beam spectrometers only require radiation that passes directly through the atomized sample, while double-beam spectrometers Figure 1.12, as implied by the name, require two beams of light; one that passes directly through the sample, and one that does not pass through the sample at all. (Insert diagrams) The single-beam spectrometers have less optical components and therefore suffer less radiation loss. Double-beam monochromators have more optical components, but they are also more stable over time because they can compensate for changes more readily.

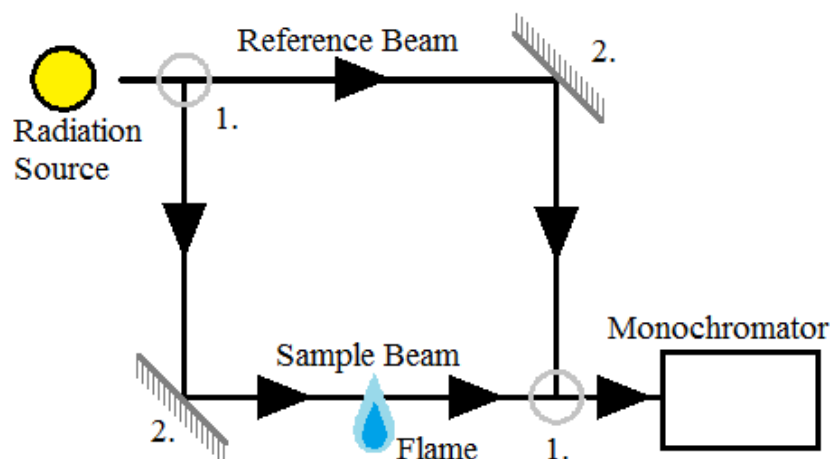


Figure 1.12: A schematic of a double-beam spectrometer showing the 50/50 beam splitters (1) and the mirrors (2).

1.1.4 Obtaining measurements

1.1.4.1 Sample preparation

Sample preparation is extremely varied because of the range of samples that can be analyzed. Regardless of the type of sample, certain considerations should be made. These include the laboratory environment, the vessel holding the sample, storage of the sample, and pretreatment of the sample.

Sample preparation begins with having a clean environment to work in. AAS is often used to measure trace elements, in which case contamination can lead to severe error. Possible equipment includes laminar flow hoods, clean rooms, and closed, clean vessels for transportation of the sample. Not only must the sample be kept clean, it also needs to be conserved in terms of pH, constituents, and any other properties that could alter the contents.

When trace elements are stored, the material of the vessel walls can adsorb some of the analyte leading to poor results. To correct for this, perfluoroalkoxy polymers (PFA), silica, glassy carbon, and other materials with inert surfaces are often used as the storage material. Acidifying the solution with hydrochloric or nitric acid can also help prevent ions from adhering to the walls of the vessel by competing for the space. The vessels should also contain a minimal surface area in order to minimize possible adsorption sites.

Pretreatment of the sample is dependent upon the nature of the sample. See Table 1.1 for sample pretreatment methods.

Sample	Examples	Pretreatment method
<i>continued on next page</i>		

Aqueous solutions	Water, beverages, urine, blood	Digestion if interference causing substituents are present
Suspensions	Water, beverages, urine, blood	Solid matter must either be removed by filtration, centrifugation or digestion, and then the methods for aqueous solutions can be followed
Organic liquids	Fuels, oils	Either direct measurement with AAS or dilution with organic material followed by measurement with AAS, standards must contain the analyte in the same form as the sample
Solids	Foodstuffs, rocks	Digestion followed by electrothermal AAS

Table 1.1: Sample pretreatment methods for AAS.

1.1.4.2 Calibration curve

In order to determine the concentration of the analyte in the solution, calibration curves can be employed. Using standards, a plot of concentration versus absorbance can be created. Three common methods used to make calibration curves are the standard calibration technique, the bracketing technique, and the analyte addition technique.

1.1.4.2.1 Standard calibration technique

This technique is the both the simplest and the most commonly used. The concentration of the sample is found by comparing its absorbance or integrated absorbance to a curve of the concentration of the standards versus the absorbances or integrated absorbances of the standards. In order for this method to be applied the following conditions must be met:

- Both the standards and the sample must have the same behavior when atomized. If they do not, the matrix of the standards should be altered to match that of the sample.
- The error in measuring the absorbance must be smaller than that of the preparation of the standards.
- The samples must be homogeneous.

The curve is typically linear and involves at least five points from five standards that are at equidistant concentrations from each other Figure 1.13. This ensures that the fit is acceptable. A least means squares calculation is used to linearly fit the line. In most cases, the curve is linear only up to absorbance values of 0.5 to 0.8. The absorbance values of the standards should have the absorbance value of a blank subtracted.

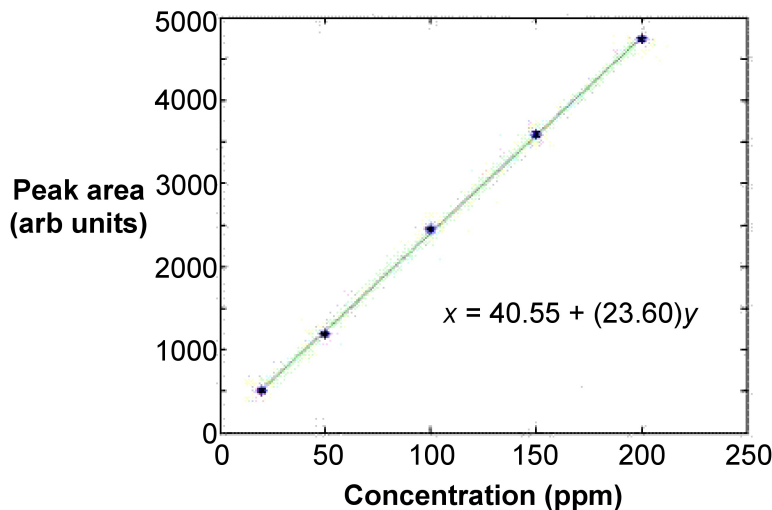


Figure 1.13: An example of a calibration curve made for the standard calibration technique.

1.1.4.2.2 Bracketing technique

The bracketing technique is a variation of the standard calibration technique. In this method, only two standards are necessary with concentrations c_1 and c_2 . They bracket the approximate value of the sample concentration very closely. Applying (1.4) to determines the value for the sample, where c_x and A_x are the concentration and adsorbance of the unknown, and A_1 and A_2 are the adsorbance for c_1 and c_2 , respectively.

$$c_x = \frac{(A_x - A_1)(c_1 - c_2)}{A_2 - A_1} + c_1 \quad (1.4)$$

This method is very useful when the concentration of the analyte in the sample is outside of the linear portion of the calibration curve because the bracket is so small that the portion of the curve being used can be portrayed as linear. Although this method can be used accurately for nonlinear curves, the further the curve is from linear the greater the error will be. To help reduce this error, the standards should bracket the sample very closely.

1.1.4.2.3 Analyte addition technique

The analyte addition technique is often used when the concomitants in the sample are expected to create many interferences and the composition of the sample is unknown. The previous two techniques both require that the standards have a similar matrix to that of the sample, but that is not possible when the matrix is unknown. To compensate for this, the analyte addition technique uses an aliquot of the sample itself as the matrix. The aliquots are then spiked with various amounts of the analyte. This technique must be used only within the linear range of the absorbances.

1.1.4.3 Measurement interference

Interference is caused by contaminants within the sample that absorb at the same wavelength as the analyte, and thus can cause inaccurate measurements. Corrections can be made through a variety of methods such

as background correction, addition of chemical additives, or addition of analyte Table 1.2.

Interference type	Cause of interference	Result	Example	Correction measures
Atomic line overlap	Spectral profile of two elements are within 0.01 nm of each other	Higher experimental absorption value than the real value	Very rare, with the only plausible problem being that of copper (324.754 nm) and europium (324.753 nm)	Typically doesn't occur in practical situations, so there is no established correction method
Molecular band and line overlap	Spectral profile of an element overlaps with molecular band	Higher experimental absorption value than the real value	Calcium hydroxide and barium at 553.6 nm in a air-acetylene flame	Background correction
Ionization (vapor-phase or cation enhancement)	atoms are ionized at the temperature of the flame/furnace, which decreases the amount of free atoms	Lower experimental absorption value than real value	Problems commonly occur with cesium, potassium, and sodium	Add an ionization suppressor (or buffer) to both the sample and the standards
Light scattering	Solid particles scatter the beam of light lowering the intensity of the beam entering the monochromator	Higher experimental absorption value than the real value	High in samples with many refractory elements, highest at UV wavelengths (add specific example)	Matrix modification and/or background correction
Chemical	The chemical being analyzed is contained within a compound in the analyte that is not atomized	Lower experimental absorption value than real value	Calcium and phosphate ions form calcium phosphate which is then converted to calcium pyrophosphate which is stable in high heat	Increase the temperature of the flame if flame AAS is being used, use a releasing chemical, or standard addition for electrothermal AAS
<i>continued on next page</i>				

Physical	If physical properties of the sample and the standards are different, atomization can be affected thus affecting the number of free atom population	Can vary in either direction depending upon the conditions	Viscosity differences, surface tension differences, etc	Alter the standards to have similar physical properties to the samples
Volatilization	In electrothermal atomization, interference will occur if the rate of volatilization is not the same for the sample as for the standard, which is often caused by a heavy matrix	Can vary in either direction depending upon the conditions	Chlorides are very volatile, so they need to be converted to a less volatile form. Often this is done by the addition of nitrate or sulfate. Zinc and lead are also highly problematic	Change the matrix by standard addition, or selectively volatilize components of the matrix

Table 1.2: Examples of interference in AAS.

1.1.5 Bibliography

- L. Ebron, A. Fisher and S. J. Hill, *An Introduction to Analytical Atomic Spectrometry*, Ed. E. H. Evans, Wiley, New York (1998).
- B. Welz and M. Sperling, *Atomic Absorption Spectrometry*, 3rd Ed, Wiley-VCH, New York (1999).
- J. W. Robinson, *Atomic Spectroscopy*, 2nd Ed. Marcel Dekker, Inc., New York (1996).
- K. S. Subramanian, *Water Res.*, 1995, **29**, 1827.
- M. Sakata and O. Shimoda, *Water Res.*, 1982, **16**, 231.
- J. C. Van Loon, *Analytical Atomic Absorption Spectroscopy Selected Methods*, Academic Press, New York (1980).

1.2 ICP-AES Analysis of Nanoparticles ²

1.2.1 What is ICP-AES?

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) is a spectral method used to determine very precisely the elemental composition of samples; it can also be used to quantify the elemental concentration with the sample. ICP-AES uses high-energy plasma from an inert gas like argon to burn analytes very rapidly. The color that is emitted from the analyte is indicative of the elements present, and the intensity of the spectral signal is indicative of the concentration of the elements that is present.

1.2.2 How does ICP-AES work?

ICP-AES works by the emission of photons from analytes that are brought to an excited state by the use of high-energy plasma. The plasma source is induced when passing argon gas through an alternating electric

²This content is available online at <<http://cnx.org/content/m22058/1.18/>>.

field that is created by an inductively couple coil. When the analyte is excited the electrons try to dissipate the induced energy moving to a ground state of lower energy, in doing this they emit the excess energy in the form of light. The wavelength of light emitted depends on the energy gap between the excited energy level and the ground state. This is specific to the element based on the number of electrons the element has and electron orbital's are filled. In this way the wavelength of light can be used to determine what elements are present by detection of the light at specific wavelengths.

As a simple example consider the situation when placing a piece of copper wire into the flame of a candle. The flame turns green due to the emission of excited electrons within the copper metal, as the electrons try to dissipate the energy incurred from the flame, they move to a more stable state emitting energy in the form of light. The energy gap between the excited state to the ground state (ΔE) dictates the color of the light or wavelength of the light.

$$\Delta E = h\nu$$

where h = Plank's constant, and ν is the frequency of the emitted light.

The wavelength of light is indicative of the element present. If another metal is placed in the flame such as iron a different color flame will be emitted because the electronic structure of iron is different from that of copper. This is a very simple analogy for what is happening in ICP-AES and how it is used to determine what elements are present. By detecting the wavelength of light that is emitted from the analyte one can deduce what elements are be present.

Naturally if there is a lot of the material present then there will be an accumulative effect making the intensity of the signal large. However, if there were very little materials present the signal would be low. By this rationale one can create a calibration curve from analyte solutions of known concentrations, whereby the intensity of the signal changes as a function of the concentration of the material that is present. When measuring the intensity from a sample of unknown concentration the intensity from this sample can be compared to that from the calibration curve, so this can be used to determine the concentration of the analytes within the sample.

1.2.3 ICP-AES of nanoparticles to determine elemental composition

As with any sample being studied by ICP-AES nanoparticles need to be digested so that all the atoms can be vaporized in the plasma equally. If a metal containing nanoparticle were not digested using a strong acid to bring the metals atoms into solution, the form of the particle could hinder some of the material being vaporized. The analyte would not be detected even though it is present in the sample and this would give an erroneous result. Nanoparticles are often covered with a protective layer of organic ligands and this must be removed also. Further to this the solvent used for the nanoparticles may also be an organic solution and this should be removed as it too will not be miscible in the aqueous medium.

Several organic solvents have low vapor pressures so it is relatively easy to remove the solvent by heating the samples, removing the solvent by evaporation. To remove the organic ligands that are present on the nanoparticle, choric acid can be used. This is a very strong acid and can break down the organic ligands readily. To digest the particles and get the metal into solution concentrated nitric acid is often used.

A typical protocol may use 0.5 mL of concentrated nanoparticle solution and digest this with 9.5 mL of concentrated nitric acid over the period of a few days. After which 0.5 mL of the digested solution is placed in 9.5 mL of nanopure water. The reason why nanopure water is used is because DI water or regular water will have some amount of metals ions present and these will be detected by the ICP-AES measurement and will lead to figures that are not truly representative of the analyte concentration alone. This is especially pertinent when there is a very a low concentration of metal analyte to be detected, and is even more a problem when the metal to be detected is commonly found in water such as iron. Once the nanopure water and digested solution are prepared then the sample is ready for analysis.

Another point to consider when doing ICP-AES on nanoparticles to determine chemical compositions, includes the potential for wavelength overlap. The energy that is released in the form of light is unique to each element, but elements that are very similar in atomic structure will have emission wavelengths that are very similar to one another. Consider the example of iron and cobalt, these are both transition metals and sit right beside each other on the periodic table. Iron has an emission wavelength at 238.204 nm and cobalt

has an emission wavelength at 238.892 nm. So if you were to try determine the amount of each element in an alloy of the two you would have to select another wavelength that would be unique to that element, and not have any wavelength overlap to other analytes in solution. For this case of iron and cobalt it would be wiser to use a wavelength for iron detection of 259.940 nm and a wavelength detection of 228.616 nm. Bearing this in mind a good rule of thumb is to try use the wavelength of the analyte that affords the best detection primarily. But if this value leads to a possible wavelength overlap of within 15 nm wavelength with another analyte in the solution then another choice should be made of the detection wavelength to prevent wavelength overlap from occurring.

Some people have also used the ICP-AES technique to determine the size of nanoparticles. The signal that is detected is determined by the amount of the material that is present in solution. If very dilute solutions of nanoparticles are being analyzed, particles are being analyzed one at a time, i.e., there will be one nanoparticle per droplet in the nebulizer. The signal intensity would then differ according to the size of the particle. In this way the ICP-AES technique could be used to determine the concentration of the particles in the solution as well as the size of the particles.

1.2.4 Calculations for ICP concentrations

In order to perform ICP-AES stock solutions must be prepared in dilute nitric acid solutions. To do this a concentrated solution should be diluted with nanopure water to prepare 7 wt% nitric acid solutions. If the concentrated solution is 69.8 wt% (check the assay amount that is written on the side of the bottle) then the amount to dilute the solution will be as such:

The density (d) of HNO_3 is 1.42 g/mL

Molecular weight of HNO_3 is 63.01

Concentrated percentage 69.8 wt% from assay. First you must determine the molarity of the concentrated solution,

$$\text{Molarity} = [(\%)(d)/(MW)] * 10$$

For this assay amount the figure will be thus

$$M = [(69.8)(1.42) / (63.01)] * 10$$

$$\therefore M = 15.73$$

This is the initial concentration C_I . To determine the molarity of the 7% solution will be thus:

$$M = [(7)(1.42) / (63.01)] * 10$$

$$\therefore M = 1.58$$

This is the final concentration C_F . We use these figures in the following concentration to determine the amount of dilution required to dilute the concentrated nitric acid to make it a 7% solution.

$$\text{mass}_I * \text{concentration}_I = \text{mass}_F * \text{concentration}_F$$

Now as we are talking about solutions the amount of mass will be measured in mL, and the concentration will be measured as a molarity, where M_I and M_F have been calculated above. In addition, the amount of dilute solution will be dependent on the user and how much is required by the user to complete the ICP analysis, for the sake of argument let's say that we need 10 mL of dilute solution, this is mL_F .

$$\text{mL}_I * C_I = \text{mL}_F * C_F$$

$$\therefore \text{mL}_I = [\text{mL}_F * C_F] / C_I$$

$$\text{mL}_I = [10 * 1.58] / 15.73$$

$$\therefore \text{mL}_I = 10.03 \text{ mL}$$

This means that 10.03 mL of the concentrated nitric acid (69.8%) should be diluted up to a total of 100 mL with nanopure water.

Now that you have your stock solution with the correct percentage then you can use this solution to prepare your solutions of varying concentration. Let's take the example that the stock solution that you purchase from a supplier has a concentration of 100 ppm of analyte, which is equivalent to 1 $\mu\text{g}/\text{mL}$.

In order to make your calibration curve more accurate it is important to be aware of two issues. Firstly as with all straight-line graphs, the more points that make up the line then the better the statistics is that the line is correct. But, secondly, the more points that are used to make up the straight line mean that more room for error is introduced to the system, to avoid these errors from occurring one should be very

vigilant and skilled in the use of pipetting and diluting of solutions. Especially when working with very low concentration solutions a small drop of material making the dilution above or below the exactly required amount can alter the concentration and hence affect the calibration deleteriously. The premise upon which the calculation is done is based on the same equation as earlier:

$$mL_I * C_I = mL_F * C_F$$

whereby C refers to concentration in ppm, and mL refers to mass in mL.

The choice of concentrations to make will depend on the samples and the concentration of analyte within the samples that are being analyzed. For first time users it is wise to make a calibration curve with a large range to encompass all the possible outcomes. When the user is more aware of the kind of concentrations that they are producing in their synthesis then they can narrow down the range to fit the kind of concentrations that they are anticipating.

In this example we will make concentrations ranging from 10 ppm to 0.1 ppm, with a total of five samples. In a typical ICP-AES analysis about 3 mL of solution is used, however if you have situations with substantial wavelength overlap then you may have chosen to do two separate runs and so you will need approximately 6 mL solution. In general it is wise to have at least 10 mL of solution to prepare for any eventuality that may occur. There will also be some extra amount needed for samples that are being used for the quality control check. For this reason 10 mL should be a sufficient amount to prepare of each concentration.

We can define the unknowns in the equation as follows:

C_I = concentration of concentrated solution (ppm)

C_F = desired concentration (ppm)

M_I = initial mass of material (mL)

M_F = mass of material required for dilution (mL)

The methodology adopted works as follows. Make the high concentration solution then take from that solution and dilute further to the desired concentrations that are required.

Let's say the concentration of the stock solution from the supplier is 100 ppm of analyte. First we should dilute to a concentration of 10 ppm. To make 10 mL of 10 ppm solution we should take 1 mL of the 100 ppm solution and dilute it up to 10 mL with nanopure water, now the concentration of this solution is 10 ppm. Then we can take from the 10 ppm solution and dilute this down to get a solution with 5 ppm. To do this take 5 mL of the 10 ppm solution and dilute it to 10 mL with nanopure water, then you will have a solution of 10 mL that is 5 ppm concentration. And so you can do this successively taking aliquots from each solution working your way down at incremental steps until you have a series of solutions that have concentrations ranging from 10 ppm all the way down to 0.1 ppm or lower, as required.

1.2.5 ICP-AES at work

While ICP-AES is a useful method for quantifying the presence of a single metal in a given nanoparticle, another very important application comes from the ability to determine the ratio of metals within a sample of nanoparticles.

In the following examples we can consider the bi-metallic nanoparticles of iron with copper. In a typical synthesis 0.75 mmol of $\text{Fe}(\text{acac})_3$ is used to prepare iron-oxide nanoparticle of the form Fe_3O_4 . It is possible to replace a quantity of the Fe^{n+} ions with another metal of similar charge. In this manner bi-metallic particles were made with a precursor containing a suitable metal. In this example the additional metal precursor will be $\text{Cu}(\text{acac})_2$.

Keep the total metal concentration in this example is 0.75 mmol. So if we want to see the effect of having 10% of the metal in the reaction as copper, then we will use 10% of 0.75 mmol, that is 0.075 mmol $\text{Cu}(\text{acac})_2$, and the corresponding amount of iron is 0.675 mmol $\text{Fe}(\text{acac})_3$. We can do this for successive increments of the metals until you make 100% copper oxide particles.

Subsequent Fe and Cu ICP-AES of the samples will allow the determination of Fe:Cu ratio that is present in the nanoparticle. This can be compared to the ratio of Fe and Cu that was applied as reactants. The graph Figure 1.14 shows how the percentage of Fe in the nanoparticle changes as a function of how much Fe is used as a reagent.

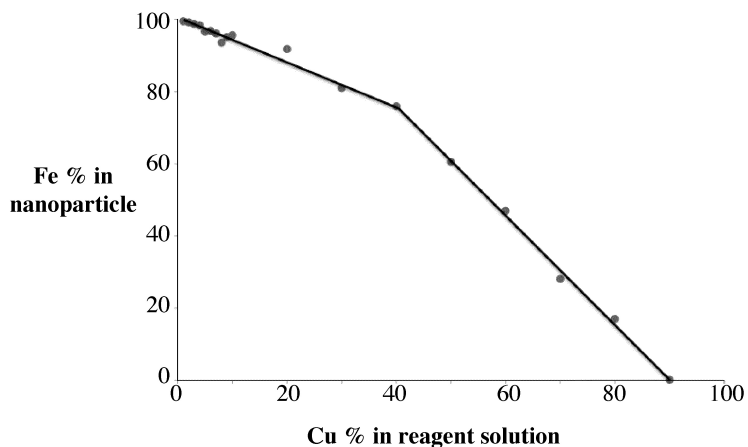


Figure 1.14: Change in iron percentage in the Fe-Cu-O nanoparticles as a function of how much iron precursor is used in the synthesis of the nanoparticles.

1.2.5.1 Determining analyte concentration

Once the nanoparticles are digested and the ICP-AES analysis has been completed you must turn the figures from the ICP-AES analysis into working numbers to determine the concentration of metals in the solution that was synthesized initially.

Let's first consider the nanoparticles that are of one metal alone. The figure given by the analysis in this case is given in units of mg/L, this is the value in ppm's. This figure was recorded for the solution that was analyzed, and this is of a dilute concentration compared to the initial synthesized solution because the particles had to be digested in acid first, then diluted further into nanopure water.

As mentioned above in the experimental 0.5 mL of the synthesized nanoparticles were first digested in 9.5 mL of concentrated nitric acid. Then when the digestion was complete 0.5 mL of this solution was dissolved in 9.5 mL of nanopure water. This was the final solution that was analyzed using ICP, and the concentration of metal in this solution will be far lower than that of the original solution. In this case the amount of analyte in the final solution being analyzed is $1/20^{\text{th}}$ that of the total amount of material in the solution that was originally synthesized.

1.2.5.2 Calculating concentration in ppm

Let us take an example that upon analysis by ICP-AES the amount of Fe detected is 6.38 mg/L. First convert the figure to mg/mL, by the following simple multiplication:

$$6.38 \text{ mg/L} * 1/1000 \text{ L/mL} = 6.38 \times 10^{-3} \text{ mg/mL}$$

The amount of material was diluted to a total volume of 10 mL. Therefore we should multiply this value by 10 mL to see how much mass was in the whole container.

$$6.38 \times 10^{-3} \text{ mg/mL} * 10 \text{ mL} = 6.38 \times 10^{-2} \text{ mg}$$

This is the total mass of iron that was present in the solution that was analyzed using the ICP device. To convert this amount to ppm we should take into consideration the fact that 0.5 mL was initially diluted to 10 mL, to do this we should divide the total mass of iron by this amount that it was diluted to.

$$6.38 \times 10^{-2} \text{ mg} / 0.5 \text{ mL} = 0.1276 \text{ mg/mL}$$

This was the total amount of analyte in the 10 mL solution that was analyzed by the ICP device, to attain the value in ppm it should be multiplied by a thousand, that is then 127.6 ppm of Fe.

1.2.5.3 Determining concentration of original solution

We now need to factor in the fact that there were several dilutions of the original solution first to digest the metals and then to dissolve them in nanopure water, in all there were two dilutions and each dilution was equivalent in mass. By diluting 0.5 mL to 10 mL, we are effectively diluting the solution by a factor of 20, and this was carried out twice.

$$0.1276 \text{ mg/mL} * 20 = 2.552 \text{ mg/mL}$$

This is the amount of analyte in the solution of digested particles, to convert this to ppm we should multiply it by 1/1000 mL/L, in the following way:

$$2.552 \text{ mg/mL} * 1/1000 \text{ mL/L} = 2552 \text{ mg/L}$$

This is essentially your answer now as 2552 ppm. This is the amount of Fe in the solution of digested particles.

This was made by diluting 0.5 mL of the original solution into 9.5 mL concentrated nitric acid, which is the same as diluting by a factor of 20. To calculate how much analyte was in the original batch that was synthesized we multiply the previous figure by 20 again.

$$2552 \text{ ppm} * 20 = 51040 \text{ ppm}$$

This is the final amount of Fe concentration of the original batch when it was synthesized and made soluble in Hexanes.

1.2.5.4 Calculating stoichiometric ratio

Moving from calculating the concentration of individual elements now we can concentrate on the calculation of stoichiometric ratios in the bi-metallic nanoparticles.

Consider the case when we have the iron and the copper elements in the nanoparticle. The amounts determined by ICP are: iron 1.429 mg/L, and copper is 1.837 mg/L.

We must account for the molecular weights of each element by dividing the ICP obtained value, by the molecular weight for that particular element. For iron this is done simply by $1.429 \text{ mg/L} / 55.85 = 0.0211$. This is molar ratio of iron.

On the other hand the ICP returns a value for copper that is $1.837 \text{ mg/L} / 63.55 = 0.0289$.

Now to determine the percentage iron we use this simple formula:

$$\% \text{Fe} = [(\text{molar ratio of iron})/(\text{sum of molar ratios})] * 100.$$

This gives a percentage value of 42.15% Fe.

To work out the copper percentage we calculate this amount using this equation:

$$\% \text{Cu} = [(\text{molar ratio of copper})/(\text{sum of molar ratios})] * 100$$

This leads to an answer of 57.85% Cu.

In this way the percentage iron in the nanoparticle can be determined as function of the reagent concentration prior to the synthesis (Figure 1.14).

1.2.5.5 Determining concentration of nanoparticles in solution

The previous examples have shown how to calculate both the concentration of one analyte and the effective shared concentration of metals in the solution. These figures pertain to the concentration of elemental atoms present in solution. To use this to determine the concentration of nanoparticles we must first consider how many atoms that are being detected are in a nanoparticle. Let us consider that the Fe_3O_4 nanoparticles are of 7 nm diameter. In a 7 nm particle we expect to find 20,000 atoms. However in this analysis we have only detected Fe atoms, so we must still account for the number of oxygen atoms that form the crystal lattice also.

For every 3 Fe atoms, there are 4 O atoms. But as iron is slightly larger than oxygen, it will make up for the fact there is one less Fe atom. This is an over simplification but at this time it serves the purpose

to make the reader aware of the steps that are required to take when judging nanoparticles concentration. Let us consider that half of the nanoparticle size is attributed to iron atoms, and the other half of the size is attributed to oxygen atoms.

As there are 20,000 atoms total in a 7 nm particle, and then when considering the effect of the oxide state we will say that for every 10,000 atoms of Fe you will have a 7 nm particle. So now we must find out how many Fe atoms are present in the sample so we can divide by 10,000 to determine how many nanoparticles are present.

In the case from above, we found the solution when synthesized had a concentration 51,040 ppm Fe atoms in solution. To determine how many atoms this equates to we will use the fact that 1 mole of material has the Avogadro number of atoms present.

$$51040 \text{ ppm} = 51040 \text{ mg/L} = 51.040 \text{ g/L}.$$

1 mole of iron weighs 55.847 g. To determine how many moles we now have, we divide the values like this:

$$(51.040 \text{ g/L}) / (55.847 \text{ g}) = 0.9139 \text{ moles / L}$$

The number of atoms is found by multiplying this by Avogadro's number:

$$(0.9139 \text{ moles/L}) * (6.022 \times 10^{23} \text{ atoms}) = 5.5 \times 10^{23} \text{ atoms/L}$$

For every 10,000 atoms we have a nanoparticle of 7 nm diameter, assuming all the particles are equivalent in size we can then divide the values:

$$(5.5 \times 10^{23} \text{ atoms/L}) / (10,000 \text{ atoms/np}) = 5.5 \times 10^{19} \text{ np/L}$$

This is the concentration of nanoparticles per liter of solution as synthesized.

1.2.5.6 Combined surface area

One very interesting thing about nanotechnology that nanoparticles can be used for is their incredible ratio between the surface areas compared with the volume. As the particles get smaller and smaller the surface area becomes more prominent. And as much of the chemistry is done on surfaces, nanoparticles are good contenders for future use where high aspect ratios are required.

In the example above we considered the particles to be of 7 nm diameters. The surface area of such a particle is $1.539 \times 10^{-16} \text{ m}^2$. So the combined surface area of all the particles is found by multiplying each particle by their individual surface areas.

$$(1.539 \times 10^{-16} \text{ m}^2) * (5.5 \times 10^{19} \text{ np/L}) = 8465 \text{ m}^2/\text{L}$$

To put this into context, an American football field is approximately 5321 m^2 . So a liter of this nanoparticle solution would have the same surface area of approximately 1.5 football fields. That is allot of area in one liter of solution when you consider how much material it would take to line the football field with thin layer of metallic iron. Remember there is only about 51 g/L of iron in this solution!

1.2.6 Bibliography

- <http://www.ivstandards.com/extras/pertable/>³
- A. Scheffer, C. Engelhard, M. Sperling, and W. Buscher, W. *Anal. Bioanal. Chem.*, 2008, **390**, 249.
- H. Nakamuru, T. Shimizu, M. Uehara, Y. Yamaguchi, and H. Maeda, *Mater. Res. Soc., Symp. Proc.*, 2007, **1056**, 11.
- S. Sun and H. Zeng, *J. Am. Chem. Soc.*, 2002, **124**, 8204.
- C. A. Crouse and A. R. Barron, *J. Mater. Chem.*, 2008, **18**, 4146.

³<http://www.ivstandards.com/extras/pertable/>

1.3 ICP-MS for Trace Metal Analysis ⁴

1.3.1 Introduction

Inductively coupled plasma mass spectroscopy (ICP-MS) is an analytical technique for determining trace multi-elemental and isotopic concentrations in liquid, solid, or gaseous samples. It combines an ion-generating argon plasma source with the sensitive detection limit of mass spectrometry detection. Although ICP-MS is used for many different types of elemental analysis, including pharmaceutical testing and reagent manufacturing, this module will focus on its applications in mineral and water studies. Although akin to ICP-AES (inductively coupled plasma atomic emission spectroscopy), ICP-MS has significant differences, which will be mentioned as well.

1.3.1.1 Basic instrumentation and operation

As shown in Figure 1.15 there are several basic components of an ICP-MS instrument, which consist of a sampling interface, a peristaltic pump leading to a nebulizer, a spray chamber, a plasma torch, a detector, an interface, and ion-focusing system, a mass-separation device, and a vacuum chamber, maintained by turbo molecular pumps. The basic operation works as follows: a liquid sample is pumped into the nebulizer to convert the sample into a spray. An internal standard, such as germanium, is pumped into a mixer along with the sample prior to nebulization to compensate for matrix effects. Large droplets are filtered out, and small droplets continue into the plasma torch, turning to ions. The mass separation device separates these ions based on their mass-to-charge ratio. An ion detector then converts these ions into an electrical signal, which is multiplied and read by computer software.

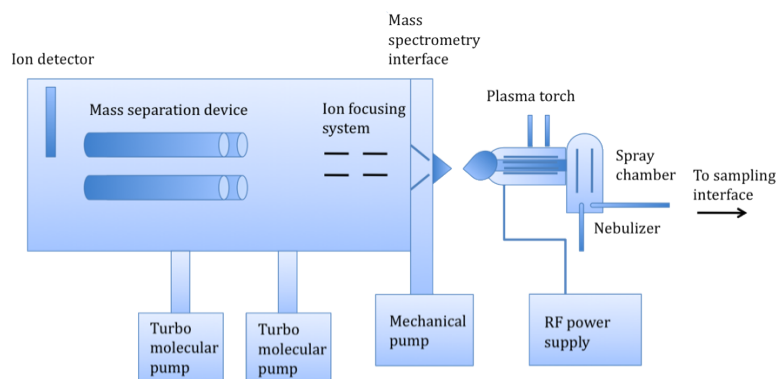


Figure 1.15: Scheme depicting the basic components of an ICP-MS system. Adapted from R. Thomas, *Practical Guide to ICP-MS: A Tutorial for Beginners*, CRC Press, Boca Raton, 2nd edn. (2008).

The main difference between ICP-MS and ICP-AES is the way in which the ions are generated and detected. In ICP-AES, the ions are excited by vertical plasma, emitting photons that are separated on the basis of their emission wavelengths. As implied by the name, ICP-MS separates the ions, generated by horizontal plasma, on the basis of their mass-to-charge ratios (m/z). In fact, caution is taken to *prevent* photons from reaching the detector and creating background noise. The difference in ion formation and detection methods has a significant impact on the relative sensitivities of the two techniques. While both methods are capable of very fast, high throughput multi-elemental analysis (~ 10 - 40 elements per minute

⁴This content is available online at <<http://cnx.org/content/m34666/1.1/>>.

per sample), ICP-MS has a detection limit of a few ppt to a few hundred ppm, compared to the ppb-ppm range (~ 1 ppb - 100 ppm) of ICP-AES. ICP-MS also works over eight orders of magnitude detection level compared to ICP-AES' six. As a result of its lower sensitivity, ICP-MS is a more expensive system. One other important difference is that only ICP-MS can distinguish between different isotopes of an element, as it segregates ions based on mass. A comparison of the two techniques is summarized in Table 1.3.

	ICP-MS	ICP-AES
Plasma	Horizontal: generates cations	Vertical: excites atoms, which emit photons
Ion detection	Mass-to-charge ratio	Wavelength of emitted light
Detection limit	1-10 ppt	1-10 ppb
Working range	8 orders of magnitude	6 orders of magnitude
Throughput	20-30 elements per minute	10-40 elements per minute
Isotope detection	Yes	No
Cost	$\sim \$150,000$	$\sim \$50,000$
Multi-element detection	Yes	Yes
Spectral interferences	Predictable, less than 300	Much greater in number and more complicated to correct
Routine accessories	Electrothermal vaporization, laser ablation, high-performance liquid chromatography, etc.	Rare

Table 1.3: Comparison of ICP-MS and ICP-AES.

1.3.1.2 Sample preparation

With such small sample sizes, care must be taken to ensure that collected samples are representative of the bulk material. This is especially relevant in rocks and minerals, which can vary widely in elemental content from region to region. Random, composite, and integrated sampling are each different approaches for obtaining representative samples.

Because ICP-MS can detect elements in concentrations as minute as a few nanograms per liter (parts per trillion), contamination is a very serious issue associated with collecting and storing samples prior to measurements. In general, use of glassware should be minimized, due to leaching impurities from the glass or absorption of analyte by the glass. If glass is used, it should be washed periodically with a strong oxidizing agent, such as chromic acid ($\text{H}_2\text{Cr}_2\text{O}_7$), or a commercial glass detergent. In terms of sample containers, plastic is usually better than glass, polytetrafluoroethylene (PTFE) and Teflon[®] being regarded as the cleanest plastics. However, even these materials can contain leachable contaminants, such as phosphorus or barium compounds. All containers, pipettes, pipette tips, and the like should be soaked in 1 - 2% HNO_3 . Nitric acid is preferred over HCl , which can ionize in the plasma to form $^{35}\text{Cl}^{16}\text{O}^+$ and $^{40}\text{Ar}^{35}\text{Cl}^+$, which have the same mass-to-charge ratios as $^{51}\text{V}^+$ and $^{75}\text{As}^+$, respectively. If possible, samples should be prepared as close as possible to the ICP-MS instrument without being in the same room.

With the exception of solid samples analyzed by laser ablation ICP-MS, samples must be in liquid or solution form. Solids are ground into a fine powder with a mortar and pestle and passed through a mesh sieve. Often the first sample is discarded to prevent contamination from the mortar or sieve. Powders are then digested with ultrapure concentrated acids or oxidizing agents, like chloric acid (HClO_3), and diluted to the correct order of magnitude with 1 - 2% trace metal grade nitric acid.

Once in liquid or solution form, the samples must be diluted with 1 - 2% ultrapure HNO_3 to a low concentration to produce a signal intensity lower than about 10^6 counts. Not all elements have the same concentration to intensity correlation; therefore, it is safer to test unfamiliar samples on ICP-AES first. Once properly diluted, the sample should be filtered through a 0.25 - 0.45 μm membrane to remove particulates.

Gaseous samples can also be analyzed by direct injection into the instrument. Alternatively, gas chromatography equipment can be coupled to an ICP-MS machine for separation of multiple gases prior to sample introduction.

1.3.1.3 Standards

Multi- and single-element standards can be purchased commercially, and must be diluted further with 1 - 2% nitric acid to prepare different concentrations for the instrument to create a calibration curve, which will be read by the computer software to determine the unknown concentration of the sample. There should be several standards, encompassing the expected concentration of the sample. Completely unknown samples should be tested on less sensitive instruments, such as ICP-AES or EDXRF (energy dispersive X-ray fluorescence), before ICP-MS.

1.3.2 Limitations of ICP-MS

While ICP-MS is a powerful technique, users should be aware of its limitations. Firstly, the intensity of the signal varies with each isotope, and there is a large group of elements that cannot be detected by ICP-MS. This consists of H, He and most gaseous elements, C, and elements without naturally occurring isotopes, including most actinides.

There are many different kinds of interferences that can occur with ICP-MS, when plasma-formed species have the same mass as the ionized analyte species. These interferences are predictable and can be corrected with element correction equations or by evaluating isotopes with lower natural abundances. Using a mixed gas with the argon source can also alleviate the interference.

The accuracy of ICP-MS is highly dependent on the user's skill and technique. Standard and sample preparations require utmost care to prevent incorrect calibration curves and contamination. As exemplified below, a thorough understanding of chemistry is necessary to predict conflicting species that can be formed in the plasma and produce false positives. While an inexperienced user may be able to obtain results fairly easily, those results may not be trustworthy. Spectral interference and matrix effects are problems that the user must work diligently to correct.

1.3.3 Applications: analysis of mineral and water samples

In order to illustrate the capabilities of ICP-MS, various geochemical applications as described. The chosen examples are representative of the types of studies that rely heavily on ICP-MS, highlighting its unique capabilities.

1.3.3.1 Trace elemental analysis of minerals

With its high throughput, ICP-MS has made sensitive analysis of multi-element detection in rock and mineral samples feasible. Studies of trace components in rock can reveal information about the chemical evolution of the mantle and crust. For example, spinel peridotite xenoliths (Figure 1.16), which are igneous rock fragments derived from the mantle, were analyzed for 27 elements, including lithium, scandium and titanium at the parts per million level and yttrium, lutetium, tantalum, and hafnium in parts per billion. X-ray fluorescence was used to complement ICP-MS, detecting metals in bulk concentrations. Both liquid and solid samples were analyzed, the latter being performed using laser-ablation ICP-MS, which points out the flexibility of the technique for being used in tandem with others. In order to prepare the solution samples, optically pure minerals were sonicated in 3 M HCl, then 5% HF, then 3 M HCl again and dissolved in distilled water. The solid samples were converted into plasma by laser ablation prior to injection into the nebulizer.

of the LA-ICP-MS instrument. The results showed good agreement between the laser ablation and solution methods. Furthermore, this comprehensive study shed light on the partitioning behavior of incompatible elements, which, due to their size and charge, have difficulty entering cation sites in minerals. In the upper mantle, incompatible trace elements, especially barium, niobium and tantalum, were found to reside in glass pockets within the peridotite samples.

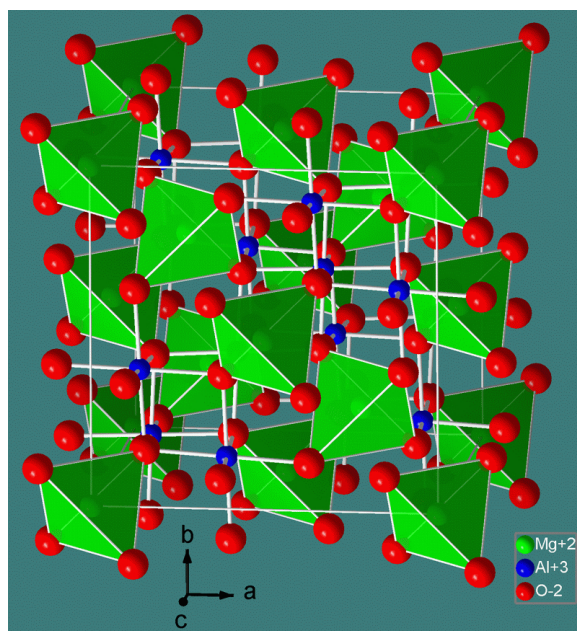


Figure 1.16: Crystal structure of a typical spinel, general formula $A^{2+}B_2^{3+}O_4^{2-}$.

1.3.3.2 Trace elemental analysis of water

Another important area of geology that requires knowledge of trace elemental compositions is water analysis. In order to demonstrate the full capability of ICP-MS as an analytical technique in this field, researchers aim to use the identification of trace metals present in groundwater to determine a fingerprint for a particular water source. In one study the analysis of four different Nevada springs determined trace metal analysis in parts per billion and even parts per trillion (ng/L). Because they were present in such low concentrations, samples containing rare earth elements lutetium, thulium, and terbium were preconcentrated by a cation exchange column to enable detection at 0.05 ppt. For some isotopes, special corrections necessary to account for false positives, which are produced by plasma-formed molecules with the same mass-to-charge ratio as the isotopic ions. For instance, false positives for Sc ($m/z = 45$) or Ti ($m/z = 47$) could result from CO_2H^+ ($m/z = 45$) or PO^+ ($m/z = 47$); and BaO^+ ($m/z = 151, 153$) conflicts with Eu-151 and Eu-153. In the latter case, barium has many isotopes (134, 135, 136, 137, 138) in various abundances, Ba-138 comprising 71.7% barium abundance. ICP-MS detects peaks corresponding to BaO^+ for all isotopes. Thus researchers were able to approximate a more accurate europium concentration by monitoring a non-interfering barium peak and extrapolating back to the concentration of barium in the system. This concentration was subtracted out to give a more realistic europium concentration. By employing such strategies, false positives could be taken into account and corrected. Additionally, 10 ppb internal standard was added to all samples to correct

for changes in sample matrix, viscosity and salt buildup throughout collection. In total, 54 elements were detected at levels spanning seven orders of magnitude. This study demonstrates the incredible sensitivity and working range of ICP-MS.

1.3.3.3 Determination of arsenic content

Elemental analysis in water is also important for the health of aquatic species, which can ultimately affect the entire food chain, including people. With this in mind, arsenic content was determined in fresh water and aquatic organisms in Hayakawa River in Kanagawa, Japan, which has very high arsenic concentrations due to its hot spring source in Owakudani Valley. While water samples were simply filtered and prior to analysis, organisms required special preparation, in order to be compatible with the sampler. Organisms collected for this studied included water bug, green macroalga, fish, and crustaceans. For total As content determination, the samples were freeze-dried to remove all water from the sample in order to know the exact final volume upon resuspension. Next, the samples were ground into a powder, followed by soaking in nitric acid, heating at 110 °C. The sample then underwent heating with hydrogen peroxide, dilution, and filtering through a 0.45 μm membrane. This protocol served to oxidize the entire sample and remove large particles prior to introduction into the ICP-MS instrument. Samples that are not properly digested can build up on the plasma torch and cause expensive damage to the instrument. Since the plasma converts the sample into various ion constituents, it is unnecessary to know the exact oxidized products prior to sample introduction. In addition to total As content, the As concentration of different organic arsenic-containing compounds (arsenicals) produced in the organisms was measured by high performance liquid chromatography coupled to ICP-MS (HPLC/ICP-MS). The arsenicals were separated by HPLC before travelling into the ICP-MS instrument for As concentration determination. For this experiment, the organic compounds were extracted from biological samples by dissolving freeze-dried samples in methanol/water solutions, sonicating, and centrifuging. The extracts were dried under vacuum, redissolved in water, and filtered prior to loading. This did not account for all compounds, however, because over 50% arsenicals were nonsoluble in aqueous solution. One important plasma side product to account for was ArCl^+ , which has the same mass-to-charge ratio ($m/z = 75$) as As. This was corrected by oxidizing the arsenic ions within the mass separation device in the ICP-MS vacuum chamber to generate AsO^+ , with m/z 91. The total arsenic concentration of the samples ranged from 17 - 18 ppm.

1.3.4 Bibliography

- R. Thomas, *Practical Guide to ICP-MS: A Tutorial for Beginners*, CRC Press, Boca Raton, 2nd edn. (2008).
- K. J. Stetzenbach, M. Amano, D. K. Creamer, and V. F. Hodge. *Ground Water*, 1994, **32**, 976.
- S. M. Eggins, R. L. Rudnick, and W. F. McDonough, *Earth Planet. Sci. Lett.*, 1998, **154**, 53.
- S. Miyashita, M. Shimoya, Y. Kamidate, T. Kuroiwa, O. Shikino, S. Fujiwara, K. A. Francesconi, and T. Kaise. *Chemosphere*, 2009, **75**, 1065.

1.4 Introduction to Combustion Analysis ⁵

1.4.1 Applications of combustion analysis

Combustion, or burning as it is more commonly known, is simply the mixing and exothermic reaction of a fuel and an oxidizer. It has been used since prehistoric times in a variety of ways, such as a source of direct heat, as in furnaces, boilers, stoves, and metal forming, or in piston engines, gas turbines, jet engines, rocket engines, guns, and explosives. Automobile engines use internal combustion in order to convert chemical into mechanical energy. Combustion is currently utilized in the production of large quantities of H_2 . Coal or

⁵This content is available online at <<http://cnx.org/content/m43578/1.1/>>.

coke is combusted at 1000 °C in the presence of water in a two-step reaction. The first step shown in (1.5) involved the partial oxidation of carbon to carbon monoxide. The second step, (1.6), involves a mixture of produced carbon monoxide with water to produce hydrogen and is commonly known as the water gas shift reaction.



Although combustion provides a multitude of uses, it was not employed as a scientific analytical tool until the late 18th century.

1.4.2 History of combustion

In the 1780's, Antoine Lavoisier (Figure 1.17) was the first to analyze organic compounds with combustion using an extremely large and expensive apparatus (Figure 1.18) that required over 50 g of the organic sample and a team of operators.



Figure 1.17: French chemist and renowned "father of modern Chemistry" Antoine Lavoisier (1743-1794).

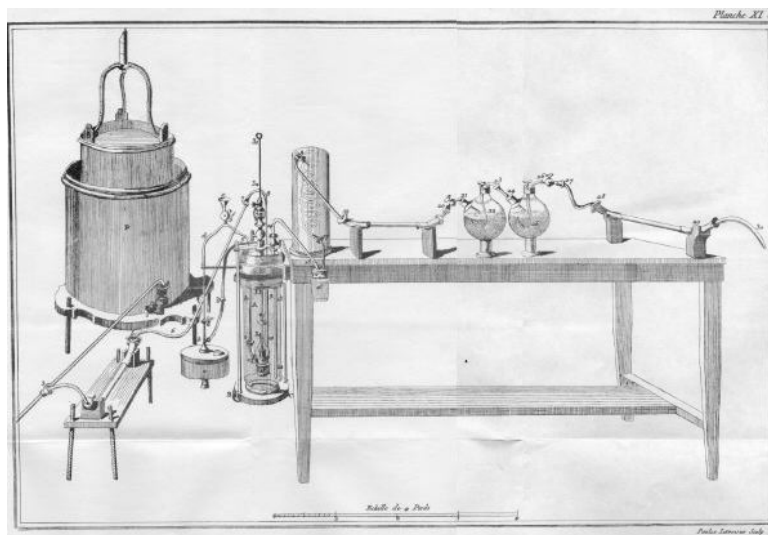


Figure 1.18: Lavoisier's combustion apparatus. A. Lavoisier, *Traité Élémentaire de Chimie*, 1789, 2, 493-501.

The method was simplified and optimized throughout the 19th and 20th centuries, first by Joseph Gay-Lussac (Figure 1.19), who began to use copper oxide in 1815, which is still used as the standard catalyst.



Figure 1.19: French chemist Joseph Gay-Lussac (1778-1850).

William Prout (Figure 1.20) invented a new method of combustion analysis in 1827 by heating a mixture of the sample and CuO using a multiple-flame alcohol lamp (Figure 1.21) and measuring the change in gaseous volume.

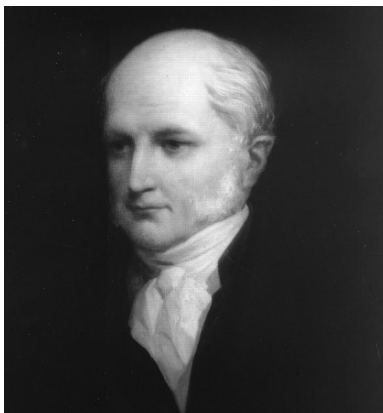


Figure 1.20: English chemist, physician, and natural theologian William Prout (1785-1850).

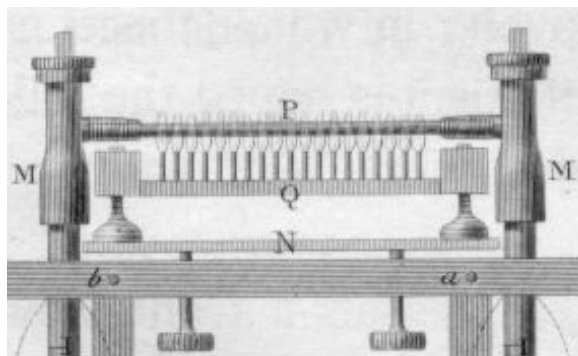


Figure 1.21: Prout's combustion apparatus. W. Prout, *Philos. T. R. Soc. Lond.*, 1827, **117**, 355.

In 1831, Justus von Liebig (Figure 1.22) simplified the method of combustion analysis into a "combustion train" system (Figure 1.23 and Figure 1.24) that linearly heated the sample using coal, absorbed water using calcium chloride, and absorbed carbon dioxide using potash (KOH). This new method only required 0.5 g of sample and a single operator, and Liebig moved the sample through the apparatus by sucking on an opening at the far right end of the apparatus.

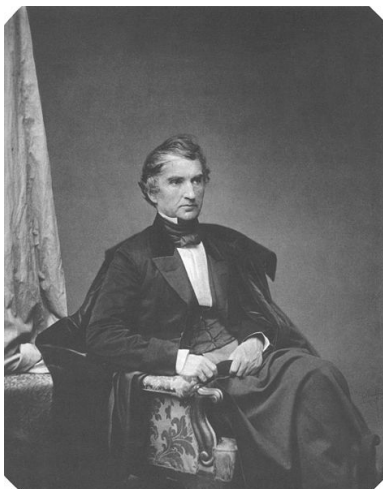


Figure 1.22: German chemist Justus von Liebig (1803-1873).

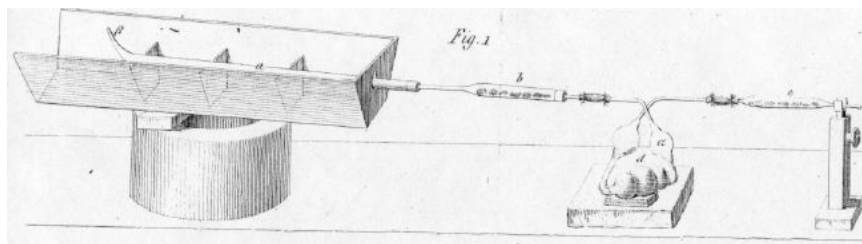


Figure 1.23: Print of von Liebig's "combustion train" apparatus for determining carbon and hydrogen composition. J. Von Liebig, *Annalen der Physik und Chemie*, 1831, 21.



Figure 1.24: Photo of von Liebig's "combustion train apparatus" for determining carbon and hydrogen composition. The Oesper Collections in the History of Chemistry, Apparatus Museum, University of Cincinnati, Case 10, Combustion Analysis. For a 360 ° view of this apparatus, visit http://digitalprojects.libraries.uc.edu/oesper/museum/case10/shelf_02/CA0010/index.php⁶.

Jean-Baptiste André Dumas (Figure 1.25) used a similar combustion train to Liebig. However, he added a U-shaped aspirator that prevented atmospheric moisture from entering the apparatus (Figure 1.26).



Figure 1.25: French chemist Jean-Baptiste André Dumas (1800-1844).

⁶http://digitalprojects.libraries.uc.edu/oesper/museum/case10/shelf_02/CA0010/index.php

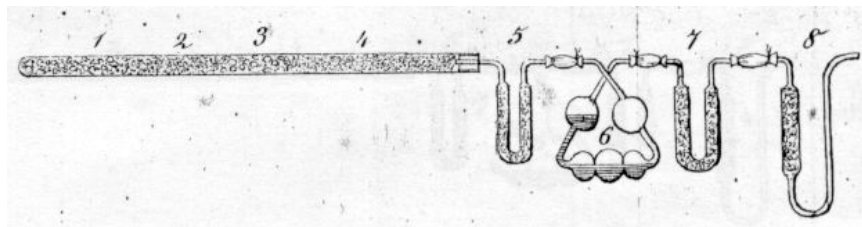


Figure 1.26: Dumas' apparatus; note the aspirator at 8. Sourced from J. A. Dumas, *Ann. der Chem. and Pharm.*, 1841, **38**, 141.

In 1923, Fritz Pregl (Figure 1.27) received the Nobel Prize for inventing a micro-analysis method of combustion. This method required only 5 mg or less, which is 0.01% of the amount required in Lavoisier's apparatus.



Figure 1.27: Austrian chemist and physician Fritz Pregl (1869-1930).

Today, combustion analysis of an organic or organometallic compound only requires about 2 mg of sample. Although this method of analysis destroys the sample and is not as sensitive as other techniques, it is still considered a necessity for characterizing an organic compound.

1.4.3 Categories of combustion

1.4.3.1 Basic flame types

There are several categories of combustion, which can be identified by their flame types (Table 1.4). At some point in the combustion process, the fuel and oxidant must be mixed together. If these are mixed before being burned, the flame type is referred to as a premixed flame, and if they are mixed simultaneously with combustion, it is referred to as a nonpremixed flame. In addition, the flow of the flame can be categorized as either laminar (streamlined) or turbulent (Figure 1.28).

Fuel/oxidizer mixing	Fluid motion	Examples
Premixed	Turbulent	Spark-ignited gasoline engine, low NO_x stationary gas turbine
Premixed	Laminar	Flat flame, Bunsen flame (followed by a nonpremixed candle for $\Phi > 1$)
Nonpremixed	Turbulent	Pulverized coal combustion, aircraft turbine, diesel engine, H_2/O_2 rocket motor
Nonpremixed	Laminar	Wood fire, radiant burners for heating, candle

Table 1.4: Types of combustion systems with examples. Adapted from J. Warnatz, U. Maas, and R. W. Dibble, *Combustion: Physical and Chemical Fundamentals, Modeling and Simulation, Experiments, Pollutant Formation*, 3rd Ed., Springer, Berlin (2001).

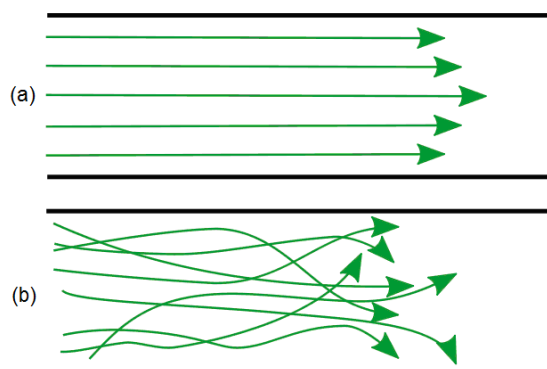


Figure 1.28: Schematic representation of (a) laminar flow and (b) turbulent flow.

The amount of oxygen in the combustion system can alter the flow of the flame and the appearance. As illustrated in Figure 1.29, a flame with no oxygen tends to have a very turbulent flow, while a flame with an excess of oxygen tends to have a laminar flow.

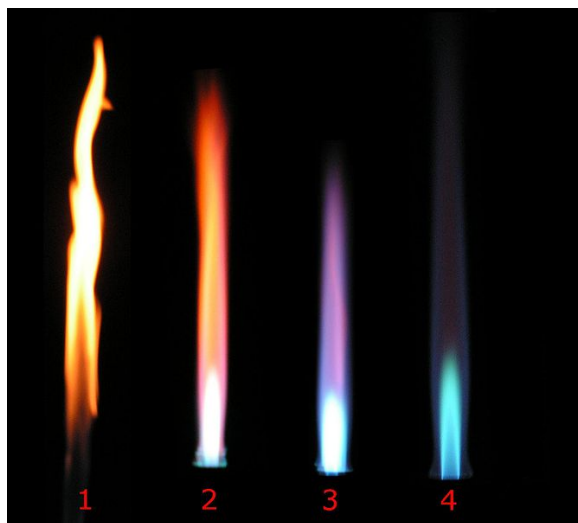


Figure 1.29: Bunsen burner flames with varying amounts of oxygen and constant amount of fuel. (1) air valve completely closed, (2) air valve slightly open, (3) air valve half open, (4) air valve completely open.

1.4.3.2 Stoichiometric combustion and calculations

A combustion system is referred to as stoichiometric when all of the fuel and oxidizer are consumed and only carbon dioxide and water are formed. On the other hand, a fuel-rich system has an excess of fuel, and a fuel-lean system has an excess of oxygen (Table 1.5).

Combustion type	Reaction example
Stoichiometric	$2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$
Fuel-rich (H_2 left over)	$3\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{H}_2$
Fuel-lean (O_2 left over)	$\text{CH}_4 + 3\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{CO}_2 + \text{O}_2$

Table 1.5: Examples of stoichiometric, fuel-rich, and fuel-lean systems.

If the reaction of a stoichiometric mixture is written to describe the reaction of exactly 1 mol of fuel (H_2 in this case), then the mole fraction of the fuel content can be easily calculated as follows, where ν denotes the mole number of O_2 in the combustion reaction equation for a complete reaction to H_2O and CO_2 , (1.7).

$$x_{\text{fuel,stoich.}} = \frac{1}{1 + \nu} \quad (1.7)$$

For example, in the reaction (1.8), the stoichiometry is determined as shown in (1.9) and (1.10).



$$\nu = 0.5 \quad (1.9)$$

$$x_{H_2,stoich} = 2/3 \quad (1.10)$$

However, as calculated this reaction would be for the reaction in an environment of pure oxygen. On the other hand, air has only 21% oxygen (78% nitrogen, 1% noble gases). Therefore, if air is used as the oxidizer, this must be taken into account in the calculations, i.e., (1.11).

$$x_{N_2} = 3.762(x_{O_2}) \quad (1.11)$$

The mole fractions for a stoichiometric mixture in air are therefore calculated in following way: (1.12) - (1.14)).

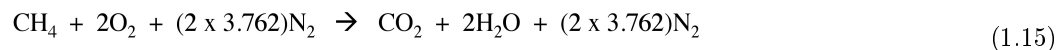
$$x_{fuel,stoich} = \frac{1}{1 + \nu(4.762)} \quad (1.12)$$

$$x_{O_2,stoich} = \nu(x_{fuel,stoich}) \quad (1.13)$$

$$x_{N_2,stoich} = 3.762(x_{O_2,stoich}) \quad (1.14)$$

Example 1.1

Calculate the fuel mole fraction (x_{fuel}) for the stoichiometric reaction:



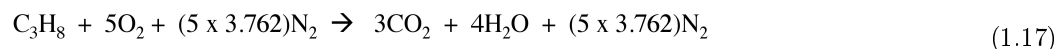
In this reaction $\nu = 2$, as 2 moles of oxygen are needed to fully oxidize methane into H_2O and CO_2 .

$$x_{fuel,stoich} = \frac{1}{1 + (2 \times 4.762)} = 0.09502 = 9.502 \text{ mol\%} \quad (1.16)$$

Exercise 1.4.1

(Solution on p. 117.)

Calculate the fuel mole fraction for the stoichiometric reaction



Premixed combustion reactions can also be characterized by the air equivalence ratio, λ , as shown in (1.18).

$$\lambda = \frac{x_{air}/x_{fuel}}{x_{air,stoich}/x_{fuel,stoich}} \quad (1.18)$$

The fuel equivalence ratio, Φ , is the reciprocal of this value (1.19).

$$\Phi = 1/\lambda \quad (1.19)$$

Rewriting (1.12) in terms of the fuel equivalence ratio gives: (1.20) - (1.23).

$$x_{fuel} = \frac{1}{1 + (\nu 4.762/\Phi)} \quad (1.20)$$

$$x_{air} = 1 - x_{fuel} \quad (1.21)$$

$$x_{O_2} = x_{air}/4.762 \quad (1.22)$$

$$x_{N_2,stoich} = 3.762(x_{O_2}) \quad (1.23)$$

The premixed combustion processes can also be identified by their air and fuel equivalence ratios (Table 1.6).

Type of combustion	Φ	λ
Rich	>1	<1
Stoichiometric	$=1$	$=1$
Lean	<1	>1

Table 1.6: Identification of combustion type by Φ and λ values.

With a premixed type of combustion, there is much greater control over the reaction. If performed at lean conditions, then high temperatures, the pollutant nitric oxide, and the production of soot can be minimized or even avoided, allowing the system to combust efficiently. However, a premixed system requires large volumes of premixed reactants, which pose a fire hazard. As a result, nonpremixed combustion, while not being efficient, is more commonly used.

1.4.4 Instrumentation

Though the instrumentation of combustion analysis has greatly improved, the basic components of the apparatus (Figure 1.30) have not changed much since the late 18th century.



Figure 1.30: Combustion apparatus from the 19th century. The Oesper Collections in the History of Chemistry, Apparatus Museum, University of Cincinnati, Case 10, Combustion Analysis. For a 360° view of this apparatus, visit http://digitalprojects.libraries.uc.edu/oesper/museum/case10/shelf_03/CA0012/index.php⁷.

⁷http://digitalprojects.libraries.uc.edu/oesper/museum/case10/shelf_03/CA0012/index.php

The sample of an organic compound, such as a hydrocarbon, is contained within a furnace or exposed to a flame and burned in the presence of oxygen, creating water vapor and carbon dioxide gas (Figure 1.31). The sample moves first through the apparatus to a chamber in which H_2O is absorbed by a hydrophilic substance and second through a chamber in which CO_2 is absorbed. The change in weight of each chamber is determined to calculate the weight of H_2O and CO_2 . After the masses of H_2O and CO_2 have been determined, they can be used to characterize and calculate the composition of the original sample.

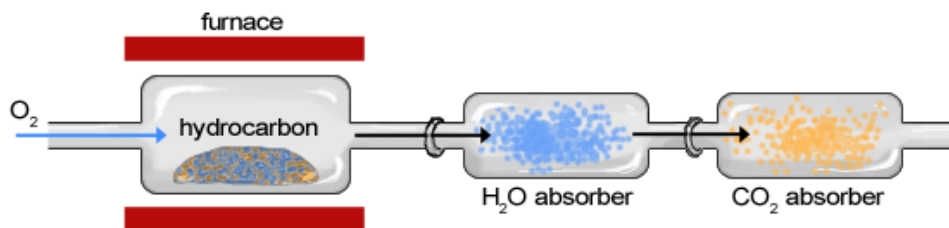


Figure 1.31: Typical modern combustion apparatus with a furnace.

1.4.5 Calculations and determining chemical formulas

1.4.5.1 Hydrocarbons

Combustion analysis is a standard method of determining a chemical formula of a substance that contains hydrogen and carbon. First, a sample is weighed and then burned in a furnace in the presence of excess oxygen. All of the carbon is converted to carbon dioxide, and the hydrogen is converted to water in this way. Each of these are absorbed in separate compartments, which are weighed before and after the reaction. From these measurements, the chemical formula can be determined.

Generally, the following reaction takes place in combustion analysis:



Example 1.2

After burning 1.333 g of a hydrocarbon in a combustion analysis apparatus, 1.410 g of H_2O and 4.305 g of CO_2 were produced. Separately, the molar mass of this hydrocarbon was found to be 204.35 g/mol. Calculate the empirical and molecular formulas of this hydrocarbon.

Step 1: Using the molar masses of water and carbon dioxide, determine the moles of hydrogen and carbon that were produced.

$$1.410\text{g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.015 \text{ g H}_2\text{O}} \times \frac{2 \text{ mol H}}{1 \text{ mol H}_2\text{O}} = 0.1565 \text{ mol H} \quad (1.25)$$

$$4.3051 \text{ g CO}_2 \times \frac{1 \text{ mol CO}_2}{44.010 \text{ g CO}_2} \times \frac{1 \text{ mol C}}{1 \text{ mol CO}_2} = 0.09782 \text{ mol C} \quad (1.26)$$

Step 2: Divide the larger molar amount by the smaller molar amount. In some cases, the ratio is not made up of two integers. Convert the numerator of the ratio to an improper fraction and

rewrite the ratio in whole numbers as shown.

$$\frac{0.1565 \text{ mol H}}{0.09782 \text{ mol C}} = \frac{1.600 \text{ mol H}}{1 \text{ mol C}} = \frac{13/5 \text{ mol H}}{1 \text{ mol C}} = \frac{8/5 \text{ mol H}}{1 \text{ mol C}} = \frac{8 \text{ mol H}}{5 \text{ mol C}} \quad (1.27)$$

Therefore, the empirical formula is C_5H_8 .

Step 3: To get the molecular formula, divide the experimental molar mass of the unknown hydrocarbon by the empirical formula weight.

$$\frac{\text{Molar mass}}{\text{Empirical formula weight}} = \frac{204.35 \text{ g/mol}}{68.114 \text{ g/mol}} = 3 \quad (1.28)$$

Therefore, the molecular formula is $(\text{C}_5\text{H}_8)_3$ or $\text{C}_{15}\text{H}_{24}$.

Exercise 1.4.2

(Solution on p. 117.)

After burning 1.082 g of a hydrocarbon in a combustion analysis apparatus, 1.583 g of H_2O and 3.315 g of CO_2 were produced. Separately, the molar mass of this hydrocarbon was found to be 258.52 g/mol. Calculate the empirical and molecular formulas of this hydrocarbon.

1.4.5.2 Compounds containing carbon, hydrogen, and oxygen

Combustion analysis can also be utilized to determine the empiric and molecular formulas of compounds containing carbon, hydrogen, and oxygen. However, as the reaction is performed in an environment of excess oxygen, the amount of oxygen in the sample can be determined from the sample mass, rather than the combustion data (Example 1.3, Exercise 1.4.3).

Example 1.3

A 2.0714 g sample containing carbon, hydrogen, and oxygen was burned in a combustion analysis apparatus; 1.928 g of H_2O and 4.709 g of CO_2 were produced. Separately, the molar mass of the sample was found to be 116.16 g/mol. Determine the empirical formula, molecular formula, and identity of the sample.

Step 1: Using the molar masses of water and carbon dioxide, determine the moles of hydrogen and carbon that were produced.

$$1.928 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.015 \text{ g H}_2\text{O}} \times \frac{2 \text{ mol H}}{1 \text{ mol H}_2\text{O}} = 0.2140 \text{ mol H} \quad (1.29)$$

$$4.709 \text{ g CO}_2 \times \frac{1 \text{ mol CO}_2}{44.010 \text{ g CO}_2} \times \frac{1 \text{ mol C}}{1 \text{ mol CO}_2} = 0.1070 \text{ mol C} \quad (1.30)$$

Step 2: Using the molar amounts of carbon and hydrogen, calculate the masses of each in the original sample.

$$0.2140 \text{ mol H} \times \frac{1.008 \text{ g H}}{1 \text{ mol H}} = 0.2157 \text{ g H} \quad (1.31)$$

$$0.1070 \text{ mol C} \times \frac{12.011 \text{ g C}}{1 \text{ mol C}} = 1.285 \text{ g C} \quad (1.32)$$

Step 3: Subtract the masses of carbon and hydrogen from the sample mass. Now that the mass of oxygen is known, use this to calculate the molar amount of oxygen in the sample.

$$2.0714 \text{ g sample} - 0.2157 \text{ g H} - 1.285 \text{ g C} = 0.5707 \text{ g O} \quad (1.33)$$

$$0.5707 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 0.03567 \text{ mol O} \quad (1.34)$$

Step 4: Divide each molar amount by the smallest molar amount in order to determine the ratio between the three elements.

$$\frac{0.03567 \text{ mol O}}{0.03567} = 1.00 \text{ mol O} = 1 \text{ mol O} \quad (1.35)$$

$$\frac{0.1070 \text{ mol C}}{0.03567} = 3.00 \text{ mol C} = 3 \text{ mol C} \quad (1.36)$$

$$\frac{0.2140 \text{ mol H}}{0.03567} = 5.999 \text{ mol H} = 6 \text{ mol H} \quad (1.37)$$

Therefore, the empirical formula is $\text{C}_3\text{H}_6\text{O}$.

Step 5: To get the molecular formula, divide the experimental molar mass of the unknown hydrocarbon by the empirical formula weight.

$$\frac{\text{Molar mass}}{\text{Empirical formula weight}} = \frac{116.16 \text{ g/mol}}{58.08 \text{ g/mol}} = 2 \quad (1.38)$$

Therefore, the molecular formula is $(\text{C}_3\text{H}_6\text{O})_2$ or $\text{C}_6\text{H}_{12}\text{O}_2$. Possible compound with this molecular formula are shown in (Figure 1.32).

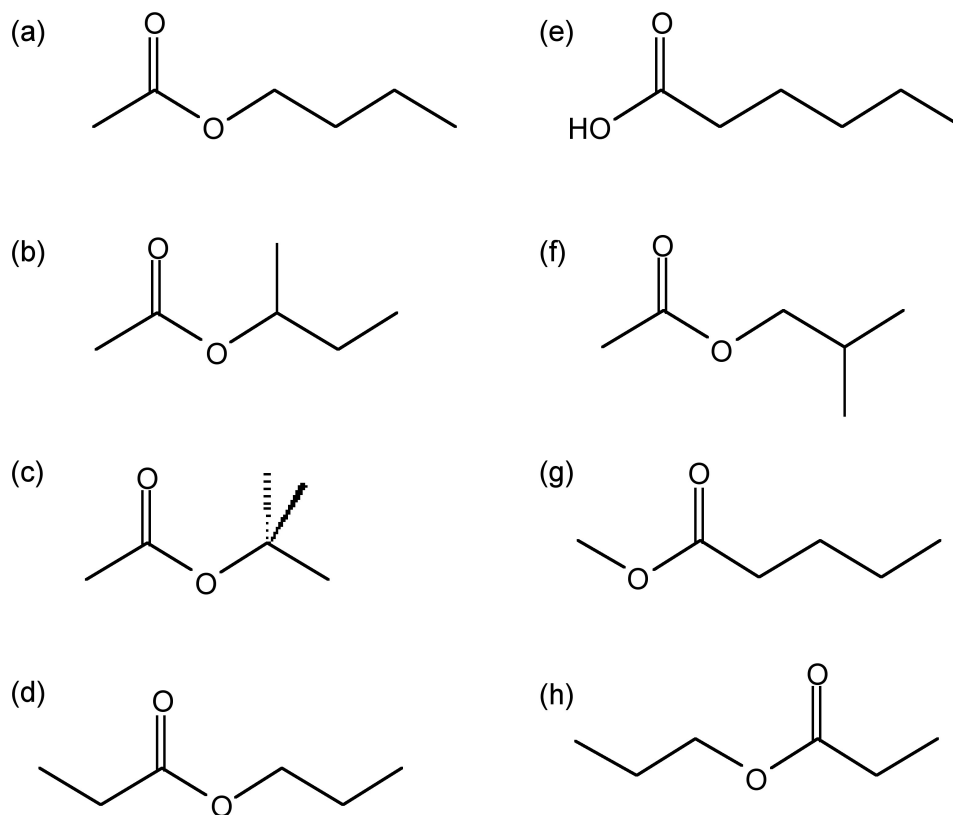


Figure 1.32: Structure of possible compounds with the molecular formula $C_6H_{12}O_2$: (a) butylacetate, (b) *sec*-butyl acetate, (c) *tert*-butyl acetate, (d) ethyl butyrate, (e) hexanoic acid, (f) isobutyl acetate, (g) methyl pentanoate, and (h) propyl propanoate.

Exercise 1.4.3

(Solution on p. 117.)

A 4.846 g sample containing carbon, hydrogen, and oxygen was burned in a combustion analysis apparatus; 4.843 g of H_2O and 11.83 g of CO_2 were produced. Separately, the molar mass of the sample was found to be 144.22 g/mol. Determine the empirical formula, molecular formula, and identity of the sample.

1.4.5.3 Binary compounds

By using combustion analysis, the chemical formula of a binary compound containing oxygen can also be determined. This is particularly helpful in the case of combustion of a metal which can result in potential oxides of multiple oxidation states.

Example 1.4

A sample of iron weighing 1.7480 g is combusted in the presence of excess oxygen. A metal oxide (Fe_xO_y) is formed with a mass of 2.4982 g. Determine the chemical formula of the oxide product and the oxidation state of Fe.

Step 1: Subtract the mass of Fe from the mass of the oxide to determine the mass of oxygen in the product.

$$2.4982 \text{ g Fe}_x\text{O}_y - 1.7480 \text{ g Fe} = 0.7502 \text{ g O} \quad (1.39)$$

Step 2: Using the molar masses of Fe and O, calculate the molar amounts of each element.

$$1.7480 \text{ g Fe} \times \frac{1 \text{ mol Fe}}{55.845 \text{ g Fe}} = 0.031301 \text{ mol Fe} \quad (1.40)$$

$$0.7502 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 0.04689 \text{ mol O} \quad (1.41)$$

Step 3: Divide the larger molar amount by the smaller molar amount. In some cases, the ratio is not made up of two integers. Convert the numerator of the ratio to an improper fraction and rewrite the ratio in whole numbers as shown.

$$\frac{0.031301 \text{ mol Fe}}{0.04689 \text{ mol O}} = \frac{0.6675 \text{ mol Fe}}{1 \text{ mol O}} = \frac{2/3 \text{ mol Fe}}{1 \text{ mol O}} = \frac{2 \text{ mol Fe}}{3 \text{ mol O}} \quad (1.42)$$

Therefore, the chemical formula of the oxide is Fe_2O_3 , and Fe has a 3+ oxidation state.

Exercise 1.4.4

(Solution on p. 117.)

A sample of copper weighing 7.295 g is combusted in the presence of excess oxygen. A metal oxide (Cu_xO_y) is formed with a mass of 8.2131 g. Determine the chemical formula of the oxide product and the oxidation state of Cu.

1.4.6 Bibliography

- J. A. Dumas, *Ann. Chem. Pharm.*, 1841, **38**, 141.
- H. Goldwhite, *J. Chem. Edu.*, 1978, **55**, 366.
- A. Lavoisier, *Traité Élémentaire de Chimie*, 1789, **2**, 493.
- J. Von Liebig, *Annalen der Physik und Chemie*, 1831, **21**, 1.
- A. Linan and F. A. Williams, *Fundamental Aspects of Combustion*, Oxford University Press, New York (1993).
- J. M. McBride, "Combustion Analysis," *Chemistry* 125, Yale University, <<http://www.chem.yale.edu/~chem125/125/history99/4RadicalsTypes/Analysis/Liebiganal.html>>.
- W. Prout, *Philos. T. R. Soc. Lond.*, 1827, **117**, 355.
- D. Shriver and P. Atkins, *Inorganic Chemistry*, 5th Ed., W. H. Freeman and Co., New York (2009).
- W. Vining et. al., *General Chemistry*, 1st Ed., Cengage, Brooks/Cole Cengage Learning, University of Massachusetts Amherst (2014).
- J. Warnatz, U. Maas, and R. W. Dibble, *Combustion: Physical and Chemical Fundamentals, Modeling and Simulation, Experiments, Pollutant Formation*, 3rd Ed., Springer, Berlin (2001).

1.5 Ion Selective Electrode ⁸

1.5.1 Introduction

Ion selective electrode (ISE) is an analytical technique used to determine the activity of ions in aqueous solution by measuring the electrical potential. ISE has many advantages compared to other techniques, including:

⁸This content is available online at <<http://cnx.org/content/m43567/1.1/>>.

1. It is relatively inexpensive and easy to operate.
2. It has wide concentration measurement range.
3. As it measure the activity, instead of concentration, it is particularly useful in biological/medical application.
4. It is a real-time measurement, which means it can monitor the change of activity of ion with time.
5. It can determine both positively and negatively charged ions.

Based on these advantages, ISE has wide variety of applications, which is reasonable considering the importance of measuring ion activity. For example, ISE finds its use in pollution monitoring in natural waters (CN^- , F^- , S^- , Cl^- , etc.), food processing (NO_3^- , NO_2^- in meat preservatives), Ca^{2+} in dairy products, and K^+ in fruit juices, etc.

1.5.2 Measurement setup

Before focusing on how ISE works, it would be good to get an idea what ISE setup looks like and the component of the ISE instrument. Figure 1.33 shows the basic components of ISE setup. It has an ion selective electrode, which allows measured ions to pass, but excludes the passage of the other ions. Within this ion selective electrode, there is an internal reference electrode (Figure 1.33), which is made of silver wire coated with solid silver chloride, embedded in concentrated potassium chloride solution (filling solution) saturated with silver chloride. This solution also contains the same ions as that to be measured. There is also a reference electrode similar to ion selective electrode, but there is no to-be-measured ion in the internal electrolyte and the selective membrane is replaced by porous frit, which allows the slow passage of the internal filling solution and forms the liquid junction with the external test solution. The ion selective electrode and reference electrode are connected by a milli-voltmeter. Measurement is accomplished simply by immersing the two electrodes in the same test solution.

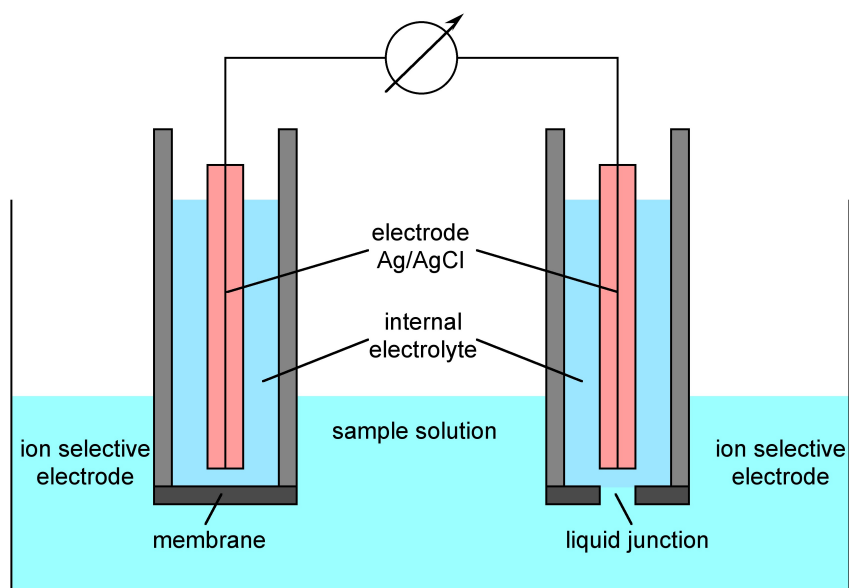


Figure 1.33: Measurement setup of ISE.

1.5.3 Theory of how ISE works

There are commonly more than one types of ions in solution. So how ISE manage to measure the concentration of certain ion in solution without being affected by other ions? This is done by applying a selective membrane at the ion selective electrode, which only allows the desired ion to go in and out. At equilibrium, there is potential difference existing between two sides of the membrane, and it is governed by the concentration of the tested solution described by Nernst equation EQ, where E is potential, E^0 is a constant characteristic of a particular ISE, R is the gas constant (8.314 J/K.mol), T is the temperature (in K), n is the charge of the ion and F is Faraday constant (96,500 coulombs/mol). To make it relevant, the measured potential difference is proportional to the logarithm of ion concentration. Thus, the relationship between potential difference and ion concentration can be determined by measuring the potential of two solutions of already-known ion concentration and a plot based on the measured potential and logarithm of the ion concentration. Based on this plot, the ion concentration of an unknown solution can be known by measuring the potential and corresponding it to the plot.

$$E = E^0 + (2.030RT/nF)\log C \quad (1.43)$$

1.5.4 Example application: determination of fluoride ion

Fluoride is added into drinking water and toothpaste to prevent dental caries and thus the determination of its concentration is of great importance to human health. Here, we will give some data and calculations to show how the concentration of fluoride ion is determined and have a glance at how relevant ISE is to our daily life. According to Nernst equation, EQ ABOVE, in this case $n = 1$, $T = 25^\circ\text{C}$ and E^0 , R , F are constants and thus this equation can be simplified as EQ.

$$E = K + S \log C \quad (1.44)$$

The first step is to obtain a calibration curve for fluoride ion and this can be done by preparing several fluoride standard solution with known concentration (Table 1.7) and making a plot of E versus $\log C$ (Figure 1.34).

Concentration (mg/L)	$\log C$	E (mV)
200.0	2.301	-35.6
100.0	2.000	-17.8
50.00	1.699	0.4
25.00	1.398	16.8
12.50	1.097	34.9
6.250	0.796	52.8
3.125	0.495	70.4
1.563	0.194	89.3
0.781	0.107	107.1
0.391	0.408	125.5
0.195	0.709	142.9

Table 1.7: Measurement results. Data from <http://zimmer.csufresno.edu/~davidz/Chem102/FluorideISE/FluorideISE.html>.

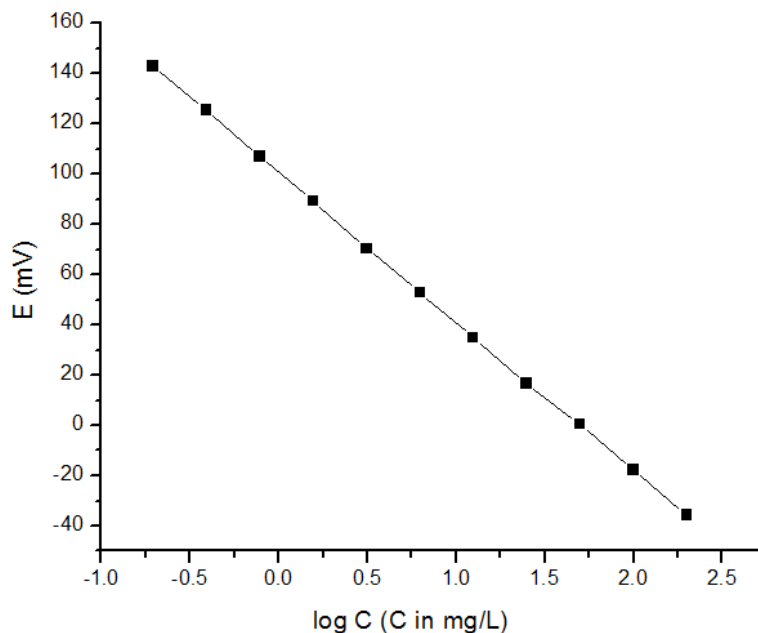


Figure 1.34: Plot of E versus log C. Based on data from <http://zimmer.csufresno.edu/~davidz/Chem102/FluorideISE/FluorideISE.html>.

From the plot in Figure 1.34, we can clearly identify the linear relationship between E versus log C with slope measured at -59.4 mV, which is very close to the theoretical value -59.2 mV at 25 °C. This plot can give the concentration of any solution containing fluoride ion within the range of 0.195 mg/L and 200 mg/L by measuring the potential of the unknown solution.

1.5.5 Limit of ISE

Though ISE is a cost-effective and useful technique, it has some drawbacks that cannot be avoided. The selective ion membrane only allows the measured ions to pass and thus the potential is only determined by this particular ion. However, the truth is there is no such membrane that only permits the passage of one ion, and so there are cases when there are more than one ions that can pass the membrane. As a result, the measured potential are affected by the passage of the “unwanted” ions. Also, because of its dependence on ion selective membrane, one ISE is only suitable for one ion and this may be inconvenient sometimes. Another problem worth noticing is that ion selective measures the concentration of ions in equilibrium at the surface of the membrane surface. This does matter much if the solution is dilute but at higher concentrations, the inter-ionic interactions between the ions in the solution tend to decrease the mobility of ions and thus the concentration near the membrane would be lower than that in the bulk. This is one source of inaccuracy of ISE. To better analyze the results of ISE, we have to be aware of these inherent limitations of it.

1.5.6 Bibliography

- D. S. Papastathopoulos and M. I. Karayannis, *J. Chem. Edu.*, 1980, **57**, 904.
- J. E. O'Reilly, *J. Chem. Edu.*, 1979, **56**, 279.

- F. Scholz, *Electroanalytical Methods: Guide to Experiments and Application*, 2nd edition, Springer, Berlin (2010).
- R. Greef, R. Peat, L. M. Peter, D. Pletcher, and J. Robinson, *Instrumental Methods in Electrochemistry*, Ellis Horwood, Chichester (1985).

1.6 A Practical Introduction to X-ray Absorption Spectroscopy ⁹

1.6.1 Introduction

X-ray absorption spectroscopy (XAS) is a technique that uses synchrotron radiation to provide information about the electronic, structural, and magnetic properties of certain elements in materials. This information is obtained when X-rays are absorbed by an atom at energies near and above the core level binding energies of that atom. Therefore, a brief description about X-rays, synchrotron radiation and X-ray absorption is provided prior to a description of sample preparation for powdered materials.

1.6.1.1 X-rays and synchrotron radiation

X-rays were discovered by the Wilhelm Röntgen in 1895 (Figure 1.35). They are a form of electromagnetic radiation, in the same manner as visible light but with a very short wavelength, around 0.25 - 25 Å. As electromagnetic radiation, X-rays have a specific energy. The characteristic range is defined by *soft* versus *hard* X-rays. *Soft* X-rays cover the range from hundreds of eV to a few KeV, and the *hard* X-rays have an energy range from a few KeV up to around 100 KeV.



Figure 1.35: German physicist Wilhelm Conrad Röntgen (1845 –1923) who received the first Nobel Prize in Physics in 1901 for the production and use of X-rays.

⁹This content is available online at <<http://cnx.org/content/m38333/1.1/>>.

X-rays are commonly produced by X-ray tubes, when high-speed electrons strike a metal target. The electrons are accelerated by a high voltage towards the metal target; X-rays are produced when the electrons collide with the nuclei of the metal target.

Synchrotron radiation is generated when particles are moving at really high velocities and are deflected along a curved trajectory by a magnetic field. The charged particles are first accelerated by a linear accelerator (LINAC) (Figure 1.36); then, they are accelerated in a booster ring that injects the particles moving almost at the speed of light into the storage ring. There, the particles are accelerated toward the center of the ring each time their trajectory is changed so that they travel in a closed loop. X-rays with a broad spectrum of energies are generated and emitted tangential to the storage ring. Beamlines are placed tangential to the storage ring to use the intense X-ray beams at a wavelength that can be selected varying the set up of the beamlines. Those are well suited for XAS measurements because the X-ray energies produced span 1000 eV or more as needed for an XAS spectrum.

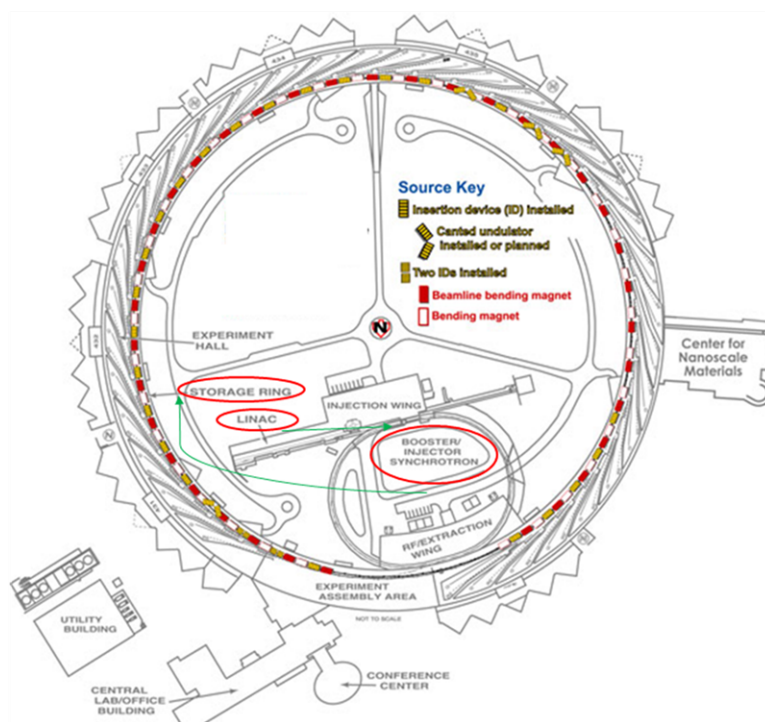


Figure 1.36: Scheme of a synchrotron and the particle trajectory inside it. Adapted from S. D. Kelly, D. Hesterberg, and B. Ravel in *Methods of Soil Analysis: Part 5, Mineralogical Methods*, Ed. A. L. Urely and R. Drees, Soil Science Society of America Book Series, Madison (2008).

1.6.1.2 X-ray absorption

Light is absorbed by matter through the photoelectric effect. It is observed when an X-ray photon is absorbed by an electron in a strongly bound core level (such as the $1s$ or $2p$ level) of an atom (Figure 1.37). In order for a particular electronic core level to participate in the absorption, the binding energy of this core level must be less than the energy of the incident X-ray. If the binding energy is greater than the energy of the

X-ray, the bound electron will not be perturbed and will not absorb the X-ray. If the binding energy of the electron is less than that of the X-ray, the electron may be removed from its quantum level. In this case, the X-ray is absorbed and any energy in excess of the electronic binding energy is given as kinetic energy to a photo-electron that is ejected from the atom.

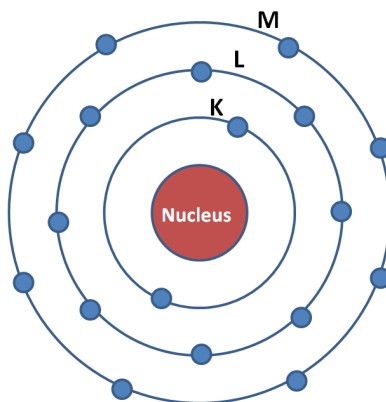


Figure 1.37: A schematic representation of the photoelectric effect when a photon with the right energy hits an electron, it is expelled.

When X-ray absorption is discussed, the primary concern is about the absorption coefficient, μ , which gives the probability that X-rays will be absorbed according to Beer's Law, (1.45), where I_0 is the X-ray intensity incident on a sample, t is the sample thickness, and I is the intensity transmitted through the sample.

$$I = I_0 e^{-\mu t} \quad (1.45)$$

The absorption coefficient, μ_E , is a smooth function of energy, with a value that depends on the sample density ρ , the atomic number Z , atomic mass A , and the X-ray energy E roughly as, (1.46).

$$\mu_E \approx \frac{\rho Z^4}{A E^3} \quad (1.46)$$

When the incident X-ray has energy equal to that of the binding energy of a core-level electron, there is a sharp rise in absorption: an absorption edge corresponding to the promotion of this core level to the continuum. For XAS, the main concern is the intensity of μ , as a function of energy, near and at energies just above these absorption edges. An XAS measurement is simply a measure of the energy dependence of μ at and above the binding energy of a known core level of a known atomic species. Since every atom has core-level electrons with well-defined binding energies, the element to probe can be selected by tuning the X-ray energy to an appropriate absorption edge. These absorption edge energies are well-known. Because the element of interest is chosen in the experiment, XAS is element-specific.

1.6.2 X-ray absorption fine structure

X-ray absorption fine structure (XAFS) spectroscopy, also named X-ray absorption spectroscopy, is a technique that can be applied for a wide variety of disciplines because the measurements can be performed on solids, gasses, or liquids, including moist or dry soils, glasses, films, membranes, suspensions or pastes, and

aqueous solutions. Despite its broad adaptability with the kind of material used, there are samples which limits the quality of an XAFS spectrum. Because of that, the sample requirements and sample preparation is reviewed in this section as well the experiment design which are vital factors in the collection of good data for further analysis.

1.6.2.1 Experiment design

The main information can be obtained using XAFS spectra consist in small changes in the absorption coefficient (E), which can be measured directly in a transmission mode or indirectly using a fluorescence mode. Therefore, a good signal to noise ratio is required (better than 10^3). In order to obtain this signal to noise ratio, an intense beam is required (on the order 10^{10} photons/second or better), with the energy bandwidth of 1 eV or less, and the capability of scanning the energy of the incident beam over a range of about 1 KeV above the edge in a time range of seconds or few minutes. As a result, synchrotron radiation is preferred further than other kind of X-ray sources previously mentioned.

1.6.2.1.1 Beamline setup

Despite the setup of a synchrotron beamline is mostly done by the assistance of specialist beamline scientists, nevertheless, it is useful to understand the system behind the measurement. The main components of a XAFS beamline, shown in Figure 1.38, are as follows:

- A harmonic rejection mirror to reduce the harmonic content of the X-ray beam.
- A monochromator to choose the X-ray energy.
- A series of slits which defines the X-ray profile.
- A sample positioning stage.
- The detectors, which can be a single ionization detector or a group of detectors to measure the X-ray intensity.

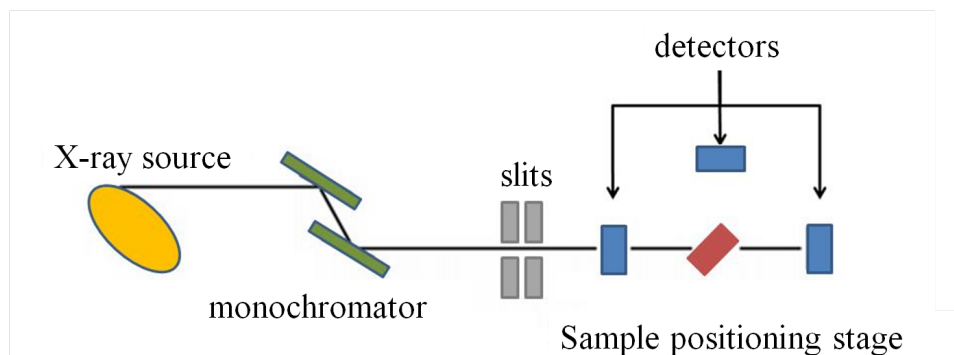


Figure 1.38: Schematic of the basic components of a XAFS beamline.

Slits are used to define the X-ray beam profile and to block unwanted X-rays. Slits can be used to increase the energy resolution of the X-ray incident on the sample at the expense of some loss in X-ray intensity. They are either fixed or adjustable slits. Fixed slits have a pre-cut opening of heights between 0.2 and 1.0 mm and a width of some centimeters. Adjustable slits use metal plates that move independently to define each edge of the X-ray beam.

1.6.2.1.1.1 Monochromator

The monochromator is used to select the X-ray energy incident on the sample. There are two main kinds of X-ray monochromators:

- 1) The double-crystal monochromator, which consists of two parallel crystals.
- 2) The channel-cut monochromator, which is a single crystal with a slot cut nearly through it.

Most monochromator crystals are made of silicon or germanium and are cut and polished such that a particular atomic plane of the crystal is parallel to the surface of the crystal as Si(111), Si(311), or Ge(111). The energy of X-rays diffracted by the crystal is controlled by rotating the crystals in the white beam.

1.6.2.1.1.2 Harmonic rejection mirrors

The harmonic X-ray intensity needs to be reduced, as these X-rays will adversely affect the XAS measurement. A common method for removing harmonic X-rays is using a harmonic rejection mirror. This mirror is usually made of Si for low energies, Rh for X-ray energies below the Rh absorption edge at 23 keV, or Pt for higher X-ray energies. The mirror is placed at a grazing angle in the beam such that the X-rays with fundamental energy are reflected toward the sample, while the harmonic X-rays are not.

1.6.2.1.1.3 Detectors

Most X-ray absorption measurements use ionization detectors. These contain two parallel plates separated by a gas-filled space that the X-rays travel through. Some of the X-rays ionize the gas particles. A voltage bias applied to the parallel plates separates the gas ions, creating a current. The applied voltage should give a linear detector response for a given change in the incident X-ray intensity. There are also other kinds as fluorescence and electron yield detectors.

1.6.2.1.2 Transmission and fluorescence modes

X-ray Absorption measurements can be performed in several modes: transmission, fluorescence and electron yield; where the two first are the most common. The choice of the most appropriate mode to use in one experiment is a crucial decision.

The transmission mode is the most used because it only implies the measure of the X-ray flux before and after the beam passes the sample. Therefore, the adsorption coefficient is defined as (1.47). Transmission experiments are standard for hard X-rays, because the use of soft X-rays implies the use the samples thinner than 1 μm . Also, this mode should be used for concentrated samples. The sample should have the right thickness and be uniform and free of pinholes.

$$\mu_E = \ln \left(\frac{I_0}{I} \right) \quad (1.47)$$

The fluorescence mode measures the incident flux I_0 and the fluorescence X-rays I_f that are emitted following the X-ray absorption event. Usually the fluorescent detector is placed at 90° to the incident beam in the horizontal plane, with the sample at an angles, commonly 45° , with respect to the beam, because in that position there is not interference generated because of the initial X-ray flux (I_0). The use of fluorescence mode is preferred for thicker samples or lower concentrations, even ppm concentrations or lower. For a highly concentrated sample, the fluorescence X-rays are reabsorbed by the absorber atoms in the sample, causing an attenuation of the fluorescence signal, it effect is named as *self-absorption* and is one of the most important concerns in the use of this mode.

1.6.3 Sample preparation for XAS

1.6.3.1 Sample requirements

1.6.3.1.1 Uniformity

The samples should have a uniform distribution of the absorber atom, and have the correct absorption for the measurement. The X-ray beam typically probes a millimeter-size portion of the sample. This volume should be representative of the entire sample.

1.6.3.1.2 Thickness.

For transmission mode samples, the thickness of the sample is really important. It supposes to be a sample with a given thickness, t , where the total adsorption of the atoms is less than 2.5 adsorption lengths, $\mu E t \approx 2.5$; and the partial absorption due to the absorber atoms is around one absorption length $\Delta \mu E t \approx 1$, which corresponds to the step edge.

The thickness to give $\Delta \mu E t = 1$ is as (1.48). where ρ is the compound density, n is the elemental stoichiometry, M is the atomic mass, σE is the adsorption cross-section in barns/atom (1 barn = 10^{-24} cm²) tabulated in McMaster tables, and E_+ and E_- are the just above and below the energy edge. This calculation can be accomplished using the free download software HEPHAESTUS.

$$t = \frac{1}{\Delta \mu} = \frac{1.66 \sum_i n_i M_i}{\rho \sum_i n_i [\sigma_i(E_+) - \sigma_i(E_-)]} \quad (1.48)$$

1.6.3.1.3 Total X-ray adsorption.

For non-concentrate samples, the total X-ray adsorption of the sample is the most important. It should be related to the area concentration of the sample (ρt , in g/cm²). The area concentration of the sample multiplied by the difference of the mass adsorption coefficient ($\Delta \mu E / \rho$) give the edge step, where a desired value to obtain a good measure is a edge step equal to one, $(\Delta \mu E / \rho) \rho t \approx 1$.

The difference of the mass adsorption coefficient is given by (1.49), where $(\mu E / \rho)$ is the mass adsorption coefficient just above (E_+) and below (E_-) of the edge energy and f_i is the mass fraction of the element i . Multiplying the area concentration, ρt , for the cross-sectional area of the sample holder, amount of sample needed is known.

$$\left(\frac{\Delta \mu E}{\rho} \right) = \sum f_i \left[\left(\frac{\mu E}{\rho} \right)_{i,(E_+)} - \left(\frac{\mu E}{\rho} \right)_{i,(E_-)} \right] \quad (1.49)$$

1.6.3.2 Sample preparation

As was described in last section, there are diluted solid samples, which can be prepared onto big substrates or concentrate solid samples which have to be prepared in *thin films*. Both methods are following described.

Liquid and gases samples can also be measured, but the preparation of those kind of sample is not discussed in this paper because it depends in the specific requirements of each sample. Several designs can be used as long they avoid the escape of the sample and the material used as container does not absorb radiation at the energies used for the measure.

1.6.3.2.1 Method 1

Step 1. The materials needed are showed in Figure 1.39: Kapton tape and film, a thin spatula, tweezers, scissors, weigh paper, mortar and pestle, and a sample holder. The sample holder can be made from several materials, as polypropylene, polycarbonate or Teflon.

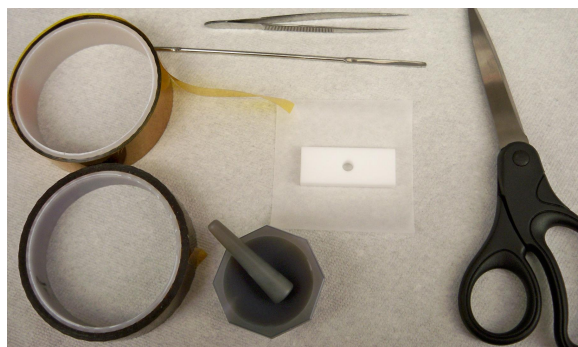


Figure 1.39: Several tools are needed for the sample preparation using Method 1.

Step 2. Two small squares of Kapton film are cut. One of them is placed onto the hole of the sample holder as shown Figure 1.40a. A piece of Kapton tape is placed onto the sample holder trying to minimize any air burble onto the surface and keeping the film as was previously placed Figure 1.40b. A side of the sample holder is now sealed in order to fill the hole (Figure 1.41).

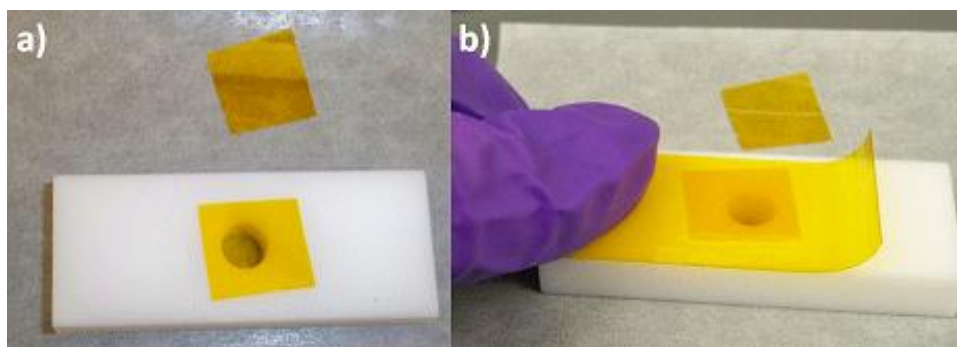


Figure 1.40: Preparing one face of the sample holder by (a) positioning a small piece of Kapton film onto the hole, which is held in place by Kapton tape (b).

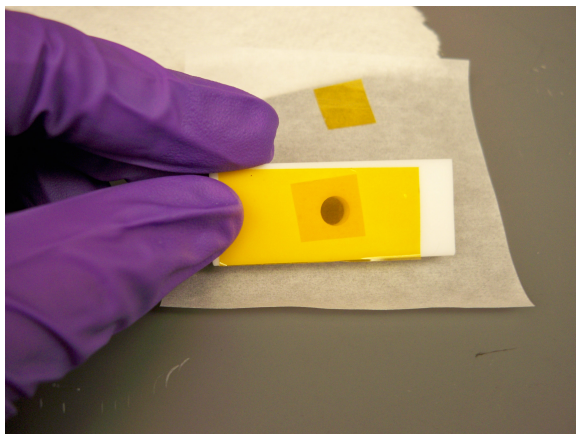


Figure 1.41: The side of the sample holder is closed.

Step 3. Before fill the sample holder, make sure your sample is a fine powder. Use the mortar to grind the sample (Figure 1.42).

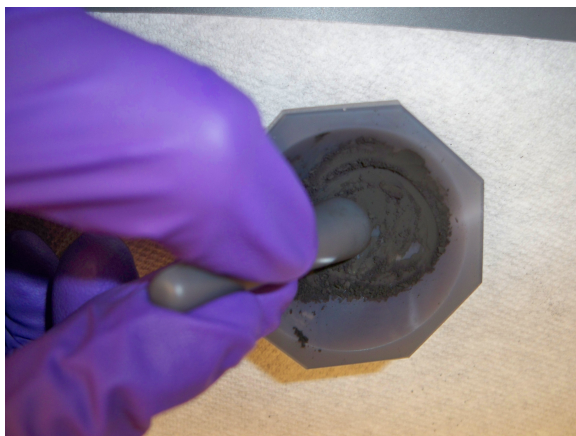


Figure 1.42: The sample is ground to be sure the grain size of the sample is homogeneous and small enough.

Step 4. Fill the hole with the powder. Make sure you have extra powder onto the hole (Figure 1.43a). With the spatula press the powder. The sample has to be as compact as possible (Figure 1.43b).

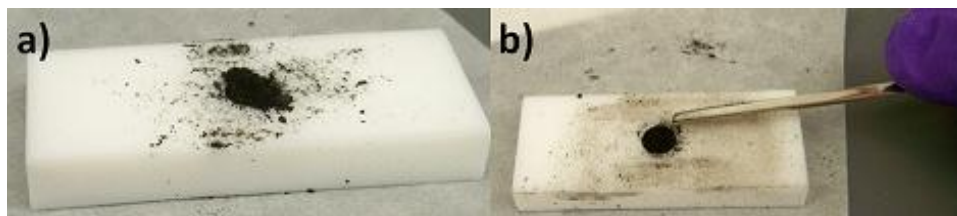


Figure 1.43: The sample holder is filled by (a) adding extra powder onto the hole then (b) compacting the sample with the spatula.

Step 5. Clean the surface of the slide. Repeat the step 2. Your sample loaded in the sample holder should look as Figure 1.44.

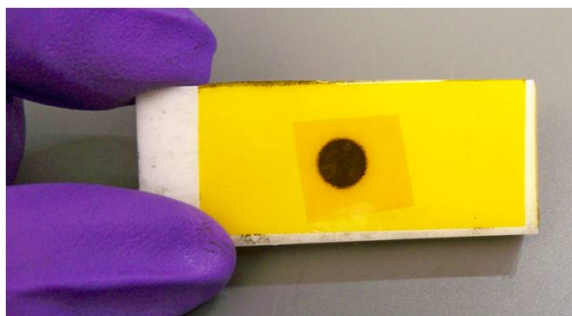


Figure 1.44: Sample loaded and sealed into the sample holder.

1.6.3.2.2 Method 2

Step 1. The materials needed are showed in Figure 1.45: Kapton tape, tweezers, scissors, weigh paper, mortar and pestle, tape and aluminum foil.

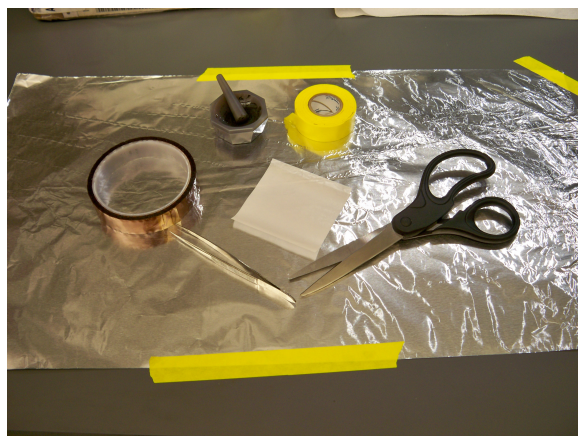


Figure 1.45: Several utensils are needed for the sample preparation using Method 2.

Step 2. Aluminum foil is placed as the work-area base. Kapton tape is place from one corner to the opposite one as shown Figure 1.46. Tape is put onto the extremes to fix it. In this case yellow tape was used in order to show where the tape should be placed but is better use Scotch invisible tape for the following steps.

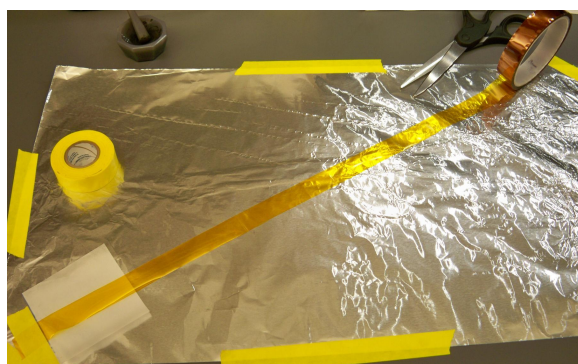


Figure 1.46: Preparation of the work-area.

Step 3. The weigh paper is placed under the Kapton tape in one of the extremes. Sample is added onto that Kapton tape extreme (Figure 1.47). The function of the weigh paper is further recuperation of extra sample.

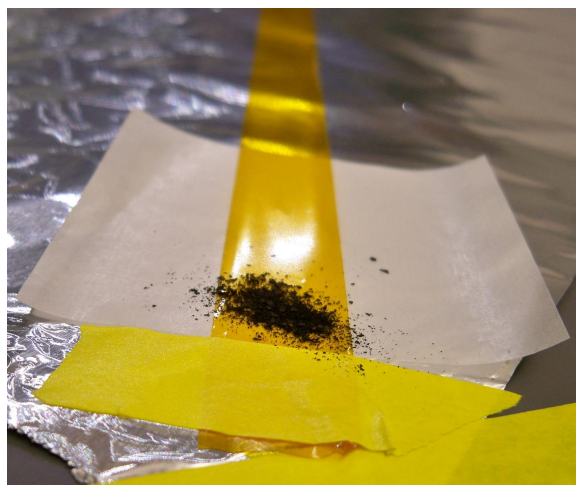


Figure 1.47: Add the sample onto an extreme of the Kapton tape.

Step 4. With one finger, the sample is dispersed along the Kapton tape, always in the same direction and taking care that the weigh paper is under the tape area is being used (Figure 1.48a). The finger should be slid several times making pressure in order to have a homogeneous and complete cover film (Figure 1.48b).

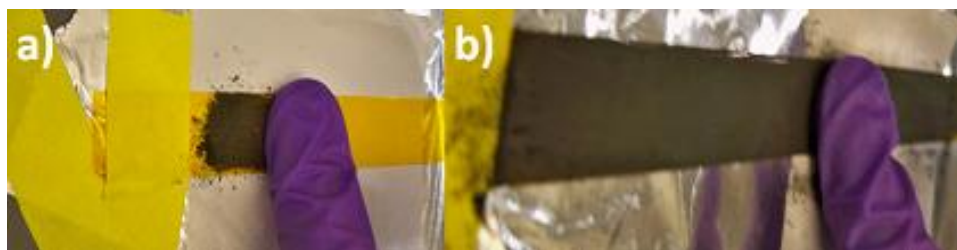


Figure 1.48: Making a thin film with a solid sample by (a) dispersing the solid along the Kapton tape and (b) repeated sliding several times to obtain a homogeneous film.

Step 5. The final sample covered Kapton tape should look like Figure 1.49. Cut the extremes in order to a further manipulation of the film.



Figure 1.49: A complete thin film.

Step 6. Using the tweezers, fold the film taking care that it is well aligned and the fold is complete plane.

Figure 1.50a shows the first folding, generating a 2 layers film. Figure 1.50b and Figure 1.50c shows the second and third folding, obtaining a 4 and 8 layers film. Sometimes a 4 layers film is good enough. You always can fold again to obtain bigger signal intensity.



Figure 1.50: Folding of the thin film simple once results in a two layer film (a) and after a second and third folding four and eight layers films are obtained (b and c, respectively).

1.6.4 Bibliography

- B. D. Cullity and S. R. Stock. *Elements of X-ray Diffraction*, Prentice Hall, Upper Saddle River (2001).
- F. Hippert, E. Geissler, J. L. Hodeau, E. Lelièvre-Berna, and J. R. Regnard. *Neutron and X-ray Spectroscopy*, Springer, Dordrecht (2006).
- G. Bunker. *Introduction to XAFS: A practical guide to X-ray Absorption Fine Structure Spectroscopy*, Cambridge University Press, Cambridge (2010).
- S. D. Kelly, D. Hesterberg, and B. Ravel in *Methods of Soil Analysis: Part 5, Mineralogical Methods*, Ed. A. L. Urely and R. Drees, Soil Science Society of America Book Series, Madison (2008).

1.7 Fluorescence Spectroscopy

1.7.1 Cold Vapor Atomic Fluorescence Spectroscopy¹⁰

1.7.1.1 Introduction

Atomic fluorescence spectroscopy (AFS) is a method that was invented by Winefordner and Vickers in 1964 as a means to analyze the chemical concentration of a sample. The idea is to excite a sample vapor with the appropriate UV radiation, and by measuring the emitting radiation, the amount of the specific element being measured could be quantified. In its most basic form, AFS consists of a UV light source to excite the sample, a monochromator, a detector and a readout device (Figure 1.51). Cold vapor atomic fluorescence spectroscopy (CVAFS) uses the same technique as AFS, but the preparation of the sample is adapted specifically to quantify the presence of heavy metals that are volatile, such as mercury, and allows for these elements to be measured at room temperature.

¹⁰This content is available online at <<http://cnx.org/content/m38339/1.1/>>.

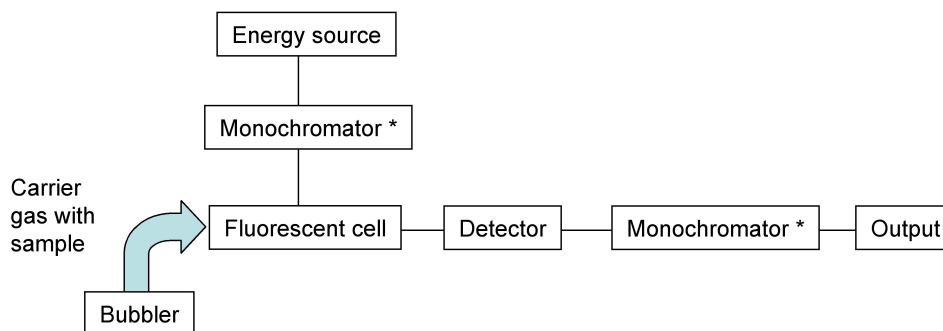


Figure 1.51: The basic setup for CVAFS. *The monochromator can be in either position in the scheme.

1.7.1.2 Theory

The theory behind CVAFS is that as the sample absorbs photons from the radiation source, it will enter an excited state. As the atom falls back into the ground state from its excited vibrational state(s), it will emit a photon, which can then be measured to determine the concentration. In its most basic sense, this process is represented by (1.50) where P_F is the power given off as photons from the sample, P_{abs} is the power of the radiation absorbed by the sample, and ϕ is the proportionality factor of the energy lost due to collisions and interactions between the atoms present, and not due to photon emission.

$$P_F = \phi P_{abs} \quad (1.50)$$

1.7.1.3 Sample preparation

For CVAFS, the sample must be digested, usually with an acid to break down the compound being tested so that all metal atoms in the sample are accessible to be vaporized. The sample is put into a bubbler, usually with an agent that will convert the element to its gaseous species. An inert gas carrier such as argon is then passed through the bubbler to carry the metal vapors to the fluorescence cell. It is important that the gas carrier is inert, so that the signal will only be absorbed and emitted by the sample in question and not the carrier gas.

1.7.1.4 Atomic fluorescence spectroscopy

Once the sample is loaded into the cell, a collimated (almost parallel) UV light source passes through the sample so that it will fluoresce. A monochromator is often used, either between the light source and the sample, or between the sample and the detector. These two different setups are referred to as excitation or emission spectrum, respectively. In an excitation spectrum, the light source is kept at a constant wavelength via the monochromator, and multiple wavelengths of emitted light are gathered, whereas in the emission spectrum, only the specified wavelength of light emitted from the sample is measured, but the sample is exposed to multiple wavelengths of light from the excitatory source. The fluorescence will be detected by a photomultiplier tube, which is extremely light sensitive, and a photodiode is used to convert the light into voltage or current, which can then in turn be interpreted into the amount of the chemical present.

1.7.1.5 Bibliography

- M. L. Bruce and D. L. Pfeil, *Am. Lab.*, 2001, 28.
- *Method 245.7: Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry*, Revision 2.0. EPA (2005).
- J. D. Winefordner and T. J. Vickers. *Anal. Chem.*, 1964, **36**, 161.

1.7.2 Detecting Mercury using Gold Amalgamation and Cold Vapor Atomic Fluorescence Spectroscopy¹¹

1.7.2.1 Introduction

Mercury poisoning can damage the nervous system, kidneys, and also fetal development in pregnant women, so it is important to evaluate the levels of mercury present in our environment. Some of the more common sources of mercury are in the air (from industrial manufacturing, mining, and burning coal), the soil (deposits, waste), water (byproduct of bacteria, waste), and in food (especially seafood). Although regulation for food, water and air mercury content differs, EPA regulation for mercury content in water is the lowest, and it cannot exceed 2 ppb (27 $\mu\text{g/L}$).

In 1972, J. F. Kopp et al. first published a method to detect minute concentrations of mercury in soil, water, and air using gold amalgamation and cold vapor atomic fluorescence spectroscopy. While atomic absorption can also measure mercury concentrations, it is not as sensitive or selective as cold vapour atomic fluorescence spectroscopy (CVAFS).

1.7.2.2 Sample preparation

As is common with all forms of atomic fluorescence spectroscopy (AFS) and atomic absorption spectrometry (AES), the sample must be digested, usually with an acid, to break down the compounds so that all the mercury present can be measured. The sample is put in the bubbler with a reducing agent such as stannous chloride (SnCl_2) so that Hg^0 is the only state present in the sample.

1.7.2.3 Gold amalgam and CVAFS

Once the mercury is in its elemental form, the argon enters the bubbler through a gold trap, and carries the mercury vapors out of the bubbler to the first gold trap, after first passing through a soda lime (mixture of Ca(OH)_2 , NaOH , and KOH) trap where any remaining acid or water vapors are caught. After all the mercury from the sample is absorbed by the first gold trap, it is heated to 450 $^\circ\text{C}$, which causes the mercury absorbed onto the gold trap to be carried by the argon gas to the second gold trap. Once the mercury from the sample has been absorbed by the second trap, it is heated to 450 $^\circ\text{C}$, releasing the mercury to be carried by the argon gas into the fluorescence cell, where light at a wavelength of 253.7 nm will be used for mercury samples. The detection limit for mercury using gold amalgamation and CVAFS is around 0.05 ng/L, but the detection limit will vary due to the equipment being used, as well as human error.

1.7.2.4 Calculating CVAFS concentrations

A standard solution of mercury should be made, and from this dilutions will be used to make at least five different standard solutions. Depending on the detection limit and what is being analyzed, the concentrations in the standard solutions will vary. Note that what other chemicals the standard solutions contain will depend upon how the sample is digested.

Example 1.5

A 1.00 g/mL Hg (1 ppm) working solution is made, and by dilution, five standards are made from the working solution, at 5.0, 10.0, 25.0, 50.0, and 100.0 ng/L (ppt). If these five standards give

¹¹This content is available online at <<http://cnx.org/content/m38307/1.1/>>.

peak heights of 10 units, 23 units, 52 units, 110 units, and 207 units, respectively, then (1.51) is used to calculate the calibration factor, where CF_x is the calibration factor, A_x is the area of the peak or peak height, and C_x is the concentration in ng/L of the standard, (1.52).

$$CF_x = A_x/C_x \quad (1.51)$$

$$10/5.0 \text{ ng/L} = 2.00 \text{ units.L/ng} \quad (1.52)$$

The calibration factors for the other four standards are calculated in the same fashion: 2.30, 2.08, 2.20, and 2.07, respectively. The average of the five calibration factors is then taken, (1.53).

$$CF_m = (2.00 + 2.30 + 2.08 + 2.20 + 2.07)/5 = 2.13 \text{ units.L/ng} \quad (1.53)$$

Now to calculate the concentration of mercury in the sample, (1.54) is used, where A_s is the area of the peak of the sample, CF_m is the mean calibration factor, V_{std} is the volume of the standard solution minus the reagents added, and V_{smp} is the volume of the initial sample (total volume minus volume of reagents added). If A_s is measured at 49 units, $V_{std} = 0.47 \text{ L}$, and $V_{smp} = 0.26 \text{ L}$, then the concentration can be calculated, (1.55).

$$[Hg] \text{ (ng/L)} = (A_s/CF_m).(V_{std}/V_{smp}) \quad (1.54)$$

$$(49 \text{ units}/2.13 \text{ units.L/ng}).(0.47 \text{ L}/0.26 \text{ L}) = 43.2 \text{ ng/L of Hg present} \quad (1.55)$$

1.7.2.5 Sources of error

Contamination from the sample collection is one of the biggest sources of error: if the sample is not properly collected or hands/gloves are not clean, this can tamper with the concentration. Also, making sure the glassware and equipment is clean from any sources of contamination.

Furthermore, sample vials that are used to store mercury-containing samples should be made out of borosilicate glass or fluoropolymer, because mercury can leach or absorb other materials, which could cause an inaccurate concentration reading.

1.7.2.6 Bibliography

- D. L. Pfeil and M. L. Bruce, *Am. Lab.*, 2001, 28.
- *Method 245.7: Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry*, Revision 2.0. EPA. 2005.
- J. D. Winefordner and T. J. Vickers, *Anal. Chem.*, 1964, **36**, 161.
- *Toxicological profile for mercury*, Agency for Toxic Substances and Disease Registry (ATSDR).
- J. F. Kopp, M. C. Longbottom, and L. B. Lobring, *AWWA*, 1972, **64**, 20.

1.7.3 The Application of Fluorescence Spectroscopy in the Mercury Ion Detection¹²

1.7.3.1 Mercury in the environment

Mercury pollution has become a global problem and seriously endangers human health. Inorganic mercury can be easily released into the environment through a variety of anthropogenic sources, such as the coal mining, solid waste incineration, fossil fuel combustion, and chemical manufacturing. It can also be released through the nonanthropogenic sources in the form of forest fires, volcanic emissions, and oceanic emission.

Mercury can be easily transported into the atmosphere as the form of the mercury vapor. The atmospheric deposition of mercury ions leads to the accumulation on plants, in topsoil, in water, and in underwater sediments. Some prokaryotes living in the sediments can convert the inorganic mercury into methylmercury, which can enter food chain and finally is ingested by human.

Mercury seriously endangers people's health. One example is that many people died due to exposure to methylmercury through seafood consumption in Minamata, Japan. Exposure in the organic mercury causes a serious of neurological problems, such as prenatal brain damage, cognitive and motion disorders, vision and hearing loss, and even death. Moreover, inorganic mercury also targets the renal epithelial cells of the kidney, which results in tubular necrosis and proteinuria.

The crisis of mercury in the environment and biological system compel people to carry out related work to confront the challenge. To design and implement new mercury detection tools will ultimately aid these endeavors. Therefore, in this paper, we will mainly introduce fluorescence molecular sensor, which is becoming more and more important in mercury detection due to its easy use, low cost and high efficiency.

1.7.3.2 Introduction of fluorescence molecular sensors

Fluorescence molecular sensor, one type of fluorescence molecular probe, can be fast, reversible response in the recognition process. There are four factors, selectivity, sensitivity, in-situ detection, and real time, that are generally used to evaluate the performance of the sensor. In this paper, four fundamental principles for design fluorescence molecular sensors are introduced.

1.7.3.2.1 Photoinduced electron transfer (PET)

Photoinduced electron transfer is the most popular principle in the design of fluorescence molecular sensors. The characteristic structure of PET sensors includes three parts as shown in Figure 1.52:

- The fluorophore absorbs the light and emits fluorescence signal.
- The receptor selectively interacts with the guest.
- A spacer connects the fluorophore and receptor together to form an integral system and successfully, effectively transfers the recognition information from receptor to fluorophore.

¹²This content is available online at <<http://cnx.org/content/m38321/1.1/>>.

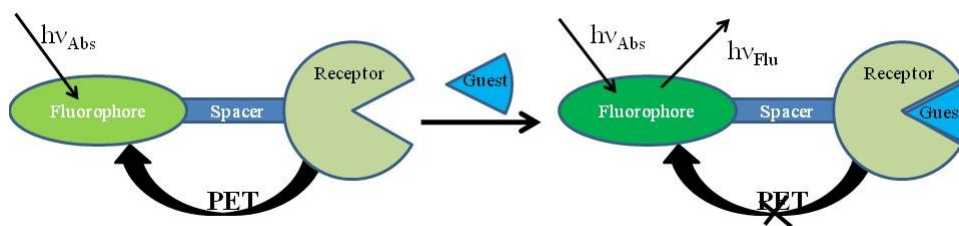


Figure 1.52: The general view of the principle of PET fluorescence molecular sensor.

In the PET sensors, photoinduced electron transfer makes the transfer of recognition information to fluorescence signal between receptor and fluorophore come true. Figure 1.52 shows the detailed process of how PET works in the fluorescence molecular sensor. The receptor could provide the electron to the vacated elector orbital of the excited fluorophore. The excited electron in the fluorophore could not come back the original orbital, resulting in the quenching of fluorescence emission. The coordination of receptor and guest decreased the electron donor ability of receptor reduced or even disrupted the PET process, then leading to the enhancement of intensity of fluorescence emission. Therefore, the sensors had weak or no fluorescence emission before the coordination. However, the intensity of fluorescence emission would increase rapidly after the coordination of receptor and guest.

1.7.3.2.2 Intramolecular charge transfer (ICT)

Intramolecular charge transfer (ICT) is also named photoinduced charge transfer. The characteristic structure of ICT sensors includes only the fluorophore and recognition group, but no spacer. The recognition group directly binds to the fluorophore. The electron withdrawing or electron donating substituents on the recognition group plays an important role in the recognition. When the recognition happens, the coordination between the recognition group and guest affects the electron density in the fluorophore, resulting in the change of fluorescence emission in the form of blue shift or red shift.

1.7.3.2.3 Excimer

When the two fluorophores are in the proper distance, an intermolecular excimer can be formed between the excited state and ground state. The fluorescence emission of the excimer is different with the monomer and mainly in the form of new, broad, strong, and long wavelength emission without fine structures. The proper distance determines the formation of excimer, therefore modulation of the distance between the two fluorophores becomes crucial in the design of the sensors based on this mechanism. The fluorophores have long lifetime in the singlet state to be easily forming the excimers. They are often used in such sensors.

1.7.3.2.4 Fluorescence resonance energy transfer (FRET)

FRET is a popular principle in the design of the fluorescence molecular sensor. In one system, there are two different fluorophores, in which one acts as a donor of excited state energy to the receptor of the other. As shown in Figure 1.53, the receptor accepts the energy from the excited state of the donor and gives the fluorescence emission, while the donor will return back to the electronic ground state. There are three factors affecting the performance of FRET. They are the distance between the donor and the acceptor, the proper

orientation between the donor emission dipole moment and acceptor absorption moment, and the extent of spectral overlap between the donor emission and acceptor absorption spectrum (Figure 1.54).

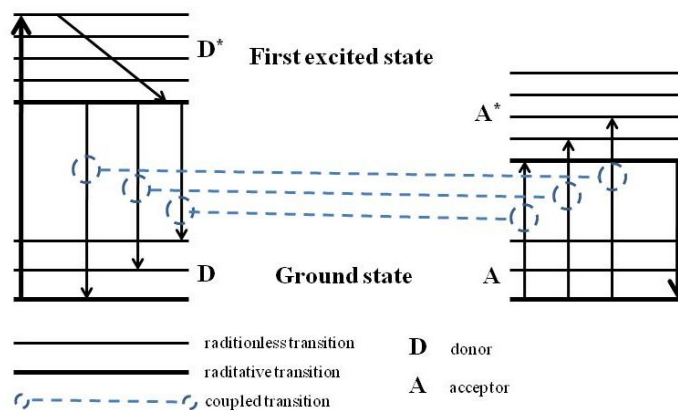


Figure 1.53: A schematic fluorescence resonance energy transfer system.

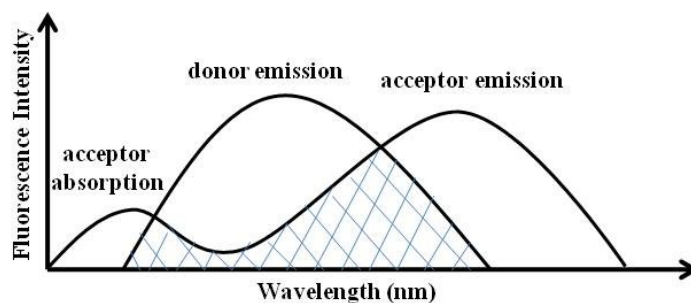


Figure 1.54: Diagram showing the spectral overlap for fluorescence resonance energy transfer system.

1.7.3.3 Introduction of fluorescence spectroscopy

1.7.3.3.1 Fluorescence

Fluorescence is a process involving the emission of light from any substance in the excited states. Generally speaking, fluorescence is the emission of electromagnetic radiation (light) by the substance absorbed the different wavelength radiation. Its absorption and emission is illustrated in the Jablonski diagram (Figure 1.55), a fluorophore is excited to higher electronic and vibrational state from ground state after excitation. The

excited molecules can relax to lower vibrational state due to the vibrational relaxation and, then further return to the ground state in the form of fluorescence emission.

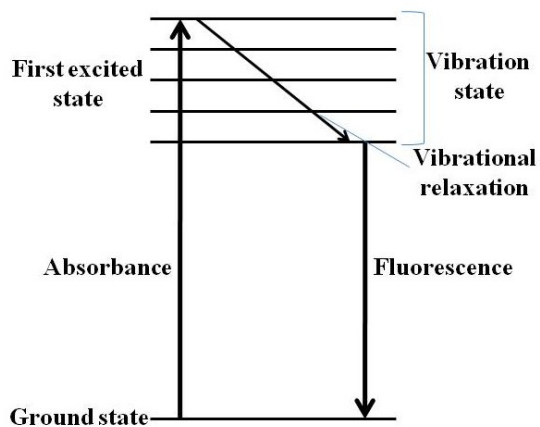


Figure 1.55: Jablonski diagram of fluorescence.

1.7.3.3.2 Instrumentation

Most spectrofluorometers can record both excitation and emission spectra. They mainly consist of four parts: light sources, monochromators, optical filters and detector (Figure 1.56).

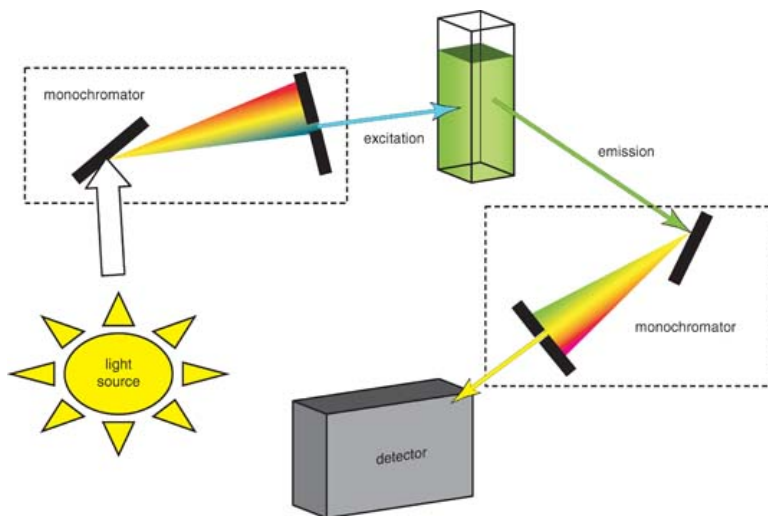


Figure 1.56: Schematic representation of a fluorescence spectrometer.

1.7.3.3.2.1 Light sources

Light sources that can emit wavelength of light over the ultraviolet and the visible range can provide the excitation energy. There are different light sources, including arc and incandescent xenon lamps, high-pressure mercury (Hg) lamps, Xe-Hg arc lamps, low pressure Hg and Hg-Ar lamps, pulsed xenon lamps, quartz-tungsten halogen (QTH) lamps, LED light sources, etc. The proper light source is chosen based on the application.

1.7.3.3.2.2 Monochromators

Prisms and diffraction gratings are two mainly used types of monochromators, which help to get the experimentally needed chromatic light with a wavelength range of 10 nm. Typically, the monochromators are evaluated based on dispersion, efficiency, stray light level and resolution.

1.7.3.3.2.3 Optical filters

Optical filters are used in addition to monochromators in order to further purifying the light. There are two kinds of optical filters. The first one is the colored filter, which is the most traditional filter and is also divided into two categories: monochromatic filter and long-pass filter. The other one is thin film filter that is the supplement for the former one in the application and being gradually instead of colored filter.

1.7.3.3.2.4 Detector

An InGaAs array is the standard detector used in many spectrofluorometers. It can provide rapid and robust spectral characterization in the near-IR.

1.7.3.4 Applications

1.7.3.4.1 PET fluorescence sensor

As a PET sensor 2-{5-[(2-{[bis-(2-ethylsulfanyl-ethyl)-amino]-methyl}-phenylamino)-methyl]-2-chloro-6-hydroxy-3-oxo-3H-xanthen-9-yl}-benzoic acid (MS1) (Figure 1.57) shows good selectivity for mercury ions in buffer solution (pH = 7, 50 mM PIPES, 100 mM KCl). From Figure 1.58, it is clear that, upon the increase of the concentration of Hg^{2+} ions, the coordination between the sensor and Hg^{2+} ions disrupted the PET process, leading to the increase of the intensity of fluorescence emission with slight red shift to 528 nm. Sensor MS1 also showed good selectivity for Hg^{2+} ions over other cations of interest as shown in the right bars in Figure 1.59; moreover, it had good resistance to the interference from other cations when detected Hg^{2+} ions in the mixture solution excluding Cu^{2+} ions as shown in the dark bars in the Figure 1.59.

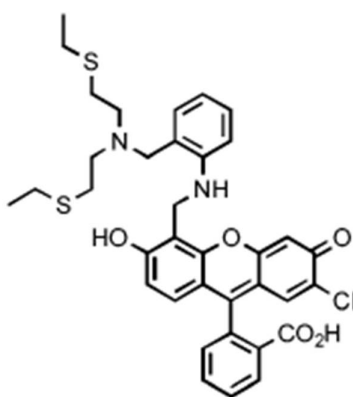


Figure 1.57: Structure of the PET fluorescence sensor 2-{5-[(2-{[bis-(2-ethylsulfanyl-ethyl)-amino]-methyl}-phenylamino)-methyl]-2-chloro-6-hydroxy-3-oxo-3H-xanthen-9-yl}-benzoic acid.

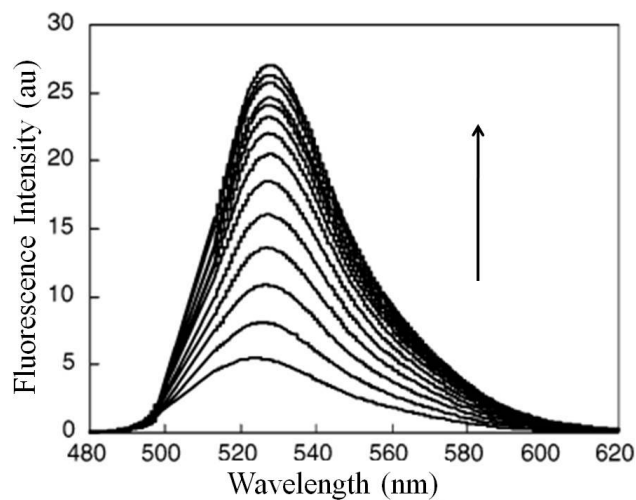


Figure 1.58: Fluorescence spectra of sensor MS1 ($1 \mu\text{M}$) upon addition of Hg^{2+} ($0 - 3 \mu\text{M}$) in buffer solution ($\text{pH} = 7$, 50 mM PIPES, 100 mM KCl) with an excitation of 500 nm .

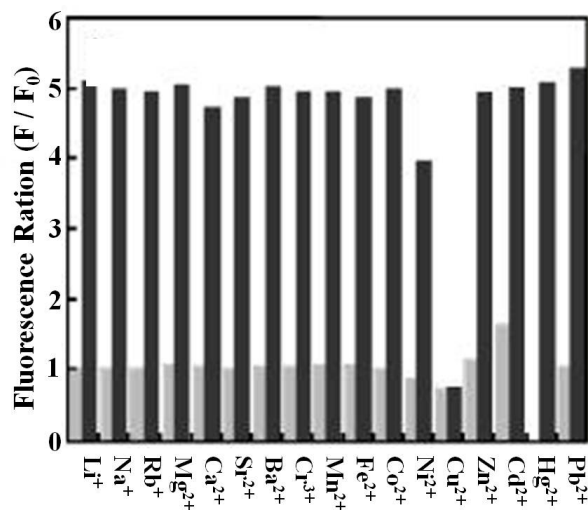


Figure 1.59: The selectivity of MS1 for Hg^{2+} ions in the presence of other cations of interest. The light bars represent the emission of MS1 in the presence of 67 equiv of the interested cations. The dark bars represent the change in integrated emission that occurs upon subsequent addition of 67 equiv of Hg^{2+} to the mixed solution.

1.7.3.4.2 ICT fluorescence sensor

2,2',2'',2'''-(3-(benzo[d]thiazol-2-yl)-2-oxo-2-H-chromene-6,7-diyl) *bis*(azanetriyl)tetrakis(N-(2-hydroxyethyl)acetamide) (RMS) (Figure 1.60) has been shown to be an ICT fluorescence sensor. From Figure 1.61, it is clear that, with the gradual increase of the concentration of Hg^{2+} ions, fluorescence emission spectra revealed a significant blue shift, which was about 100-nm emission band shift from 567 to 475 nm in the presence of 40 equiv of Hg^{2+} ions. The fluorescence change came from the coexistence of two electron-rich aniline nitrogen atoms in the electron-donating receptor moiety, which prevented Hg^{2+} ions ejection from them simultaneously in the excited ICT fluorophore. Sensor RMS also showed good selectivity over other cations of interest. As shown in Figure 1.62, it is easy to find that only Hg^{2+} ions can modulate the fluorescence of RMS in a neutral buffered water solution.

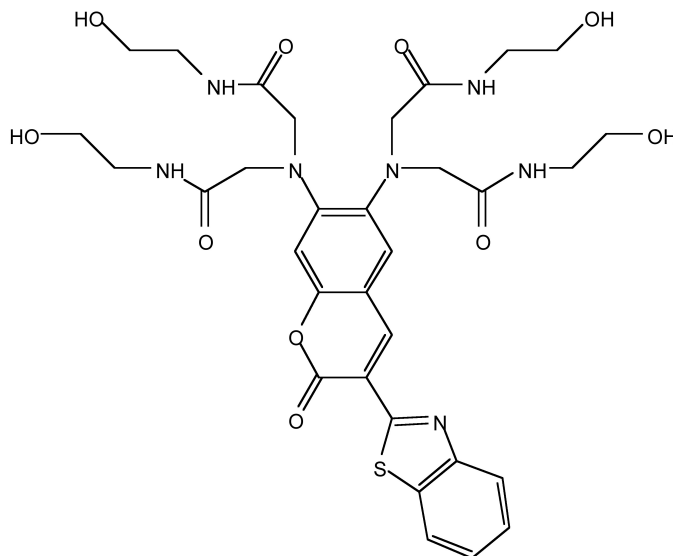


Figure 1.60: Structure of the ICT fluorescence sensor 2,2',2'',2'''-(3-(benzo[d]thiazol-2-yl)-2-oxo-2-H-chromene-6,7-diyl) *bis*(azanetriyl) tetrakis(N-(2-hydroxyethyl)acetamide) (RMS).

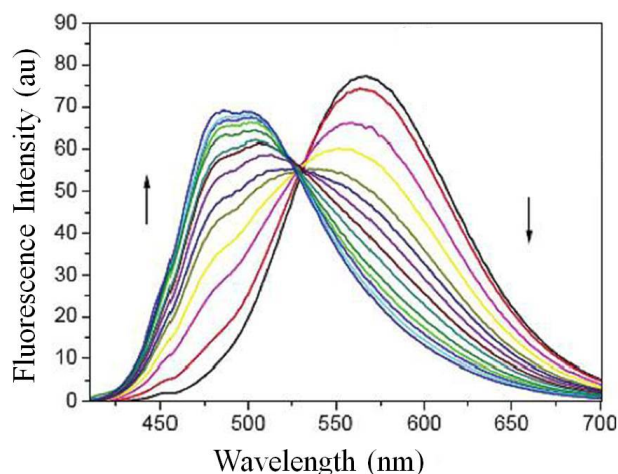


Figure 1.61: Fluorescence spectra of RMS (5 μM) upon addition of Hg^{2+} (0 μM to 200 μM) in 0.05 M phosphate-buffered water solution (pH 7.5) with an excitation of 390 nm.



Figure 1.62: Fluorescence response of 10 μM RMS in the presence of 20 equiv of different cations of interest at the same condition: control (0), Cd^{2+} (1), Hg^{2+} (2), Fe^{3+} (3), Zn^{2+} (4), Ag^+ (5), Co^{2+} (6), Cu^{2+} (7), Ni^{2+} (8), and Pb^{2+} (9).

1.7.3.4.3 Excimer fluorescence sensor

The (NE,N'E)-2,2'-(ethane-1,2-diyl-*bis*(oxy))*bis*(N-(pyren-4-ylmethylene)aniline) (BA) (Figure 1.63) is the excimer fluorescence sensor. As shown in Figure 1.64, when BA existed without mercury ions in the mixture of HEPES- CH_3CN (80:20, v/v, pH 7.2), it only had the weak monomer fluorescence emission. Upon the increase of the concentration of mercury ions in the solution of BA, a strong excimer fluorescence emission at 462 nm appeared and increased with the change of the concentration of mercury ions. From Figure 1.65, it is clear that BA showed good selectivity for mercury ions. Moreover, it had good resistance to the interference when detecting mercury ions in the mixture solution.

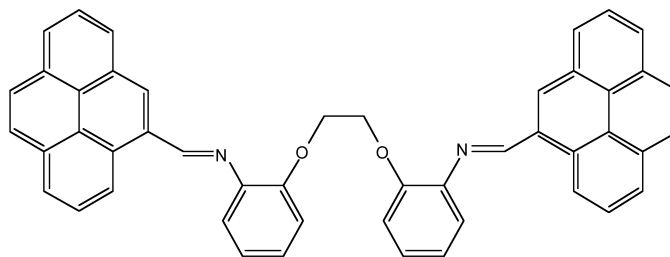


Figure 1.63: Structure of the excimer fluorescence sensor (NE,N'E)-2,2'-(ethane-1,2-diyl-bis(oxy)) bis(N-(pyren-4-ylmethylene) aniline) (BA).

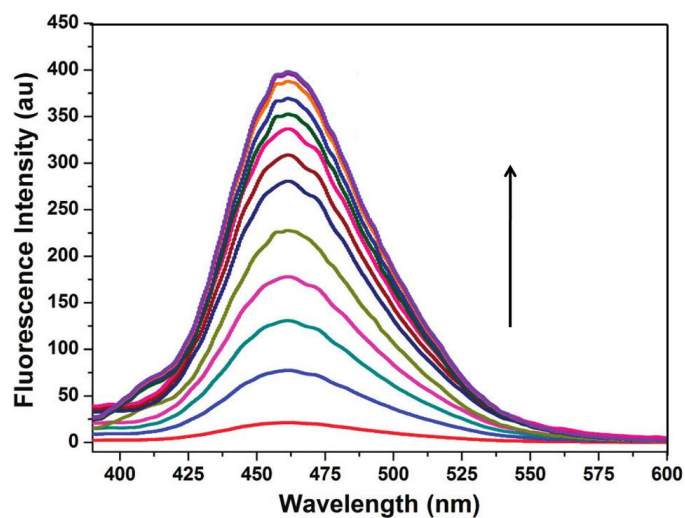


Figure 1.64: Fluorescence spectra of BA ($1 \mu\text{M}$) upon addition of Hg^{2+} ($0 \mu\text{M}$ to $10 \mu\text{M}$) in the mixture of HEPES- CH_3CN (80:20, v/v, pH 7.2) with an excitation of 365 nm.

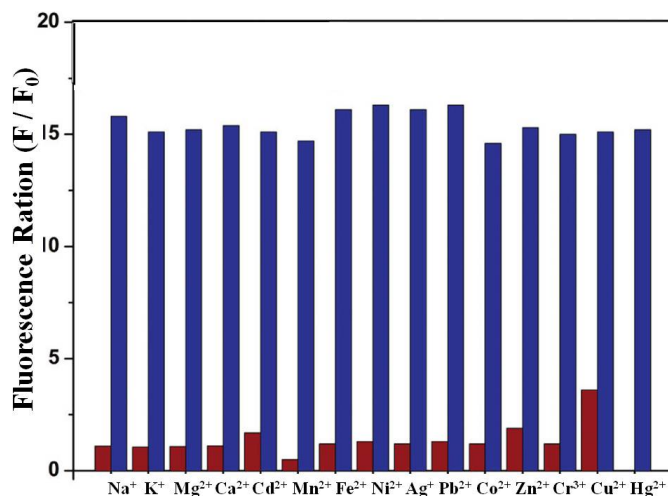


Figure 1.65: Fluorescence response of BA ($1 \mu\text{M}$) with 10 equiv of other cations of interest in the same condition. Bars represent the final (F) over the initial (F_0) integrated emission. The red bars represent the addition of the competing metal ion to a $1 \mu\text{M}$ solution of BA. The blue bars represent the change of the emission that occurs upon the subsequent addition of $10 \mu\text{M}$ Hg^{2+} to the above solution.

1.7.3.4.4 FRET fluorescence sensor

The calix[4]arene derivative bearing two pyrene and rhodamine fluorophores (CPR) (Figure 1.66) is a characteristic FRET fluorescence sensor. Fluorescence titration experiment of CPR ($10.0 \mu\text{M}$) with Hg^{2+} ions was carried out in $\text{CHCl}_3/\text{CH}_3\text{CN}$ (50:50, v/v) with an excitation of 343 nm. As shown in Figure 1.67, upon gradual increase the concentration of Hg^{2+} ions in the solution of CPR, the increased fluorescence emission of the ring-opened rhodamine at 576 nm was observed with a concomitantly declining excimer emission of pyrene at 470 nm. Moreover, an isosbestic point centered at 550 nm appeared. This change in the fluorescence emission demonstrated that an energy from the pyrene excimer transferred to rhodamine, resulting from the trigger of Hg^{2+} ions. Figure 1.68 showed that CPR had good resistance to other cations of interest when detected Hg^{2+} ions, though Pb^{2+} ions had little interference in this process.

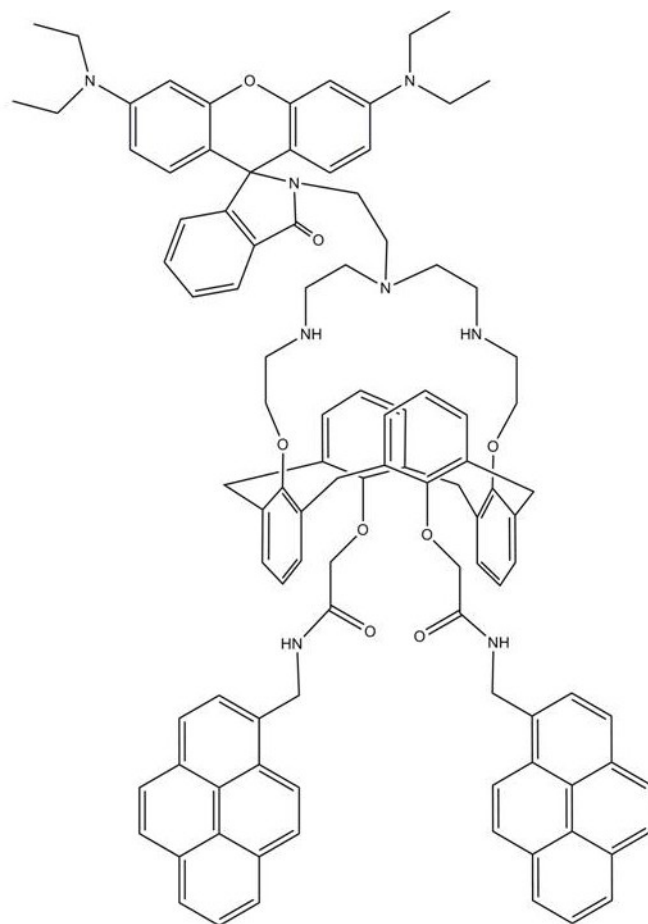


Figure 1.66: Structure of the FRET fluorescence sensor calix[4]arene derivative (CPR) bearing two pyrene and rhodamine fluorophores.

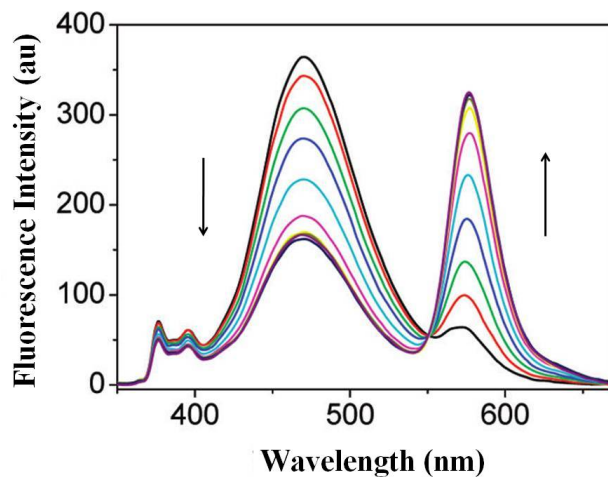


Figure 1.67: Fluorescence spectra of CPR (10.0 μM) in $\text{CHCl}_3/\text{CH}_3\text{CN}$ (50:50, v/v) upon addition of different concentrations of $\text{Hg}(\text{ClO}_4)_2$ (0 μM to 30 μM).

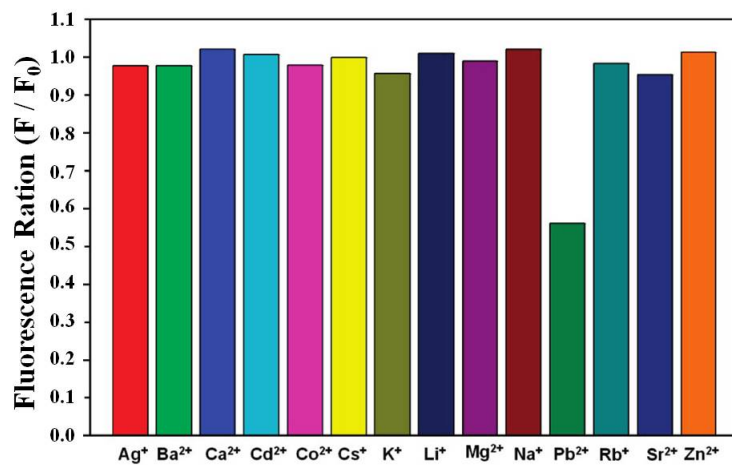


Figure 1.68: Competition experiment of 10.0 μM CPR at 576 nm with 10 equiv of other cations of interest in the presence of Hg^{2+} (3 equiv) in the same condition. F_0 and F denote the fluorescence intensity of CPR and Hg^{2+} ions and the interested metal ions in the presence of CPR and Hg^{2+} ions.

1.7.3.5 Bibliography

- E. M. Nolan and S. J. Lippard, *Chem. Rev.*, 2008, **108**, 3443.
- J. S. Kim and D. T. Quang, *Chem. Rev.*, 2007, **107**, 3780.
- E. M. Nolan and S. J. Lippard, *J. Am. Chem. Soc.*, 2003, **125**, 14270.
- J. B. Wang, X. H. Qian, and J. G. Cui, *J. Org. Chem.*, 2006, **71**, 4308.
- Y. H. Lee, M. H. Lee, J. F. Zhang, and J. S. Kim, *J. Org. Chem.*, 2010, **75**, 7159.
- Y. Zhou, C. Y. Zhu, X. S. Gao, X. Y. You, and C. Yao, *Org. Lett.*, 2010, **12**, 2566.
- J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, 3rd Edition, Springer (2006).

1.8 X-ray Photoelectron Spectroscopy

1.8.1 XPS Analysis of Modified Surfaces¹³

1.8.1.1 Introduction

X-Ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA), is one of the most widely used surface techniques in materials science and chemistry. It allows the determination of atomic composition of the sample in a non-destructive manner, as well as other chemical information, such as binding constants, oxidation states and speciation. The sample under study is subjected to irradiation by a high energy X-ray source. The X-rays penetrate only 5 – 20 Å into the sample, allowing for surface specific, rather than bulk chemical, analysis. As an atom absorbs the X-rays, the energy of the X-ray will cause a K-shell electron to be ejected, as illustrated by Figure 1.69. The K-shell is the lowest energy shell of the atom. The ejected electron has a kinetic energy (KE) that is related to the energy of the incident beam ($h\nu$), the electron binding energy (BE), and the work function of the spectrometer (ϕ) ((1.56)). Thus, the binding energy of the electron can be calculated.

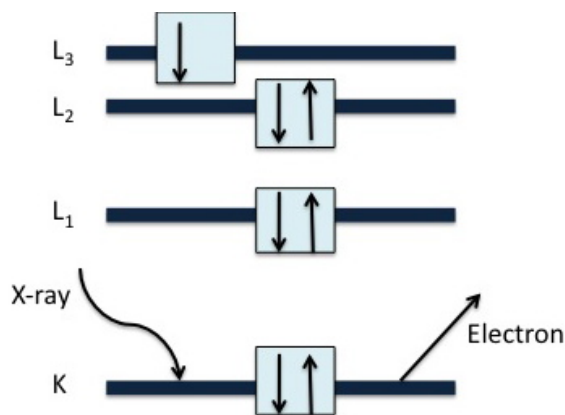


Figure 1.69: Excitation of an electron from an atom's K-shell.

$$BE = h\nu - KE - \phi_s \quad (1.56)$$

¹³This content is available online at <<http://cnx.org/content/m34527/1.1/>>.

Table 1.8 shows the binding energy of the ejected electron, and the orbital from which the electron is ejected, which is characteristic of each element. The number of electrons detected with a specific binding energy is proportional to the number of corresponding atoms in the sample. This then provides the percent of each atom in the sample.

Element	Binding energy (eV)
Carbon (C) (1s)	284.5 - 285.1
Nitrogen (N) (1s)	396.1 - 400.5
Oxygen (O) (1s)	526.2 - 533.5
Silicon (Si) (2p)	98.8 - 99.5
Sulfur (S) (2p _{3/2})	164.0 - 164.3
Iron (Fe) (2p _{3/2})	706.8 - 707.2
Gold (Au) (4f _{7/2})	83.8 - 84.2

Table 1.8: Binding energies for select elements in their elemental forms.

The chemical environment and oxidation state of the atom can be determined through the shifts of the peaks within the range expected (Table 1.9). If the electrons are shielded then it is easier, or requires less energy, to remove them from the atom, i.e., the binding energy is low. The corresponding peaks will shift to a lower energy in the expected range. If the core electrons are not shielded as much, such as the atom being in a high oxidation state, then just the opposite occurs. Similar effects occur with electronegative or electropositive elements in the chemical environment of the atom in question. By synthesizing compounds with known structures, patterns can be formed by using XPS and structures of unknown compounds can be determined.

Compound	Binding energy (eV)
COH (C 1s)	286.01 – 286.8
CHF (C 1s)	287.5 – 290.2
Nitride (N 1s)	396.2 – 398.3
Fe ₂ O ₃ (from O, 1s)	529.5 – 530.2
Fe ₂ O ₃ (from Fe, 2p _{3/2})	710.7 – 710.9
FeO (from Fe, 2p _{3/2})	709.1 – 709.5
SiO ₂ (from O, 1s)	532.5 – 533.3
SiO ₂ (from Si, 2p)	103.2 – 103.9

Table 1.9: Binding energies of electrons in various compounds.

Sample preparation is important for XPS. Although the technique was originally developed for use with thin, flat films, XPS can be used with powders. In order to use XPS with powders, a different method of sample preparation is required. One of the more common methods is to press the powder into a high purity indium foil. A different approach is to dissolve the powder in a quickly evaporating solvent, if possible, which can then be drop-casted onto a substrate. Using sticky carbon tape to adhere the powder to a disc or pressing the sample into a tablet are an option as well. Each of these sample preparations are designed to make the powder compact, as powder not attached to the substrate will contaminate the vacuum chamber. The sample also needs to be completely dry. If it is not, solvent present in the sample can destroy the necessary high vacuum and contaminate the machine, affecting the data of the current and future samples.

1.8.1.2 Analyzing functionalized surfaces

1.8.1.2.1 Depth Profiling

When analyzing a sample (Figure 1.70 a) by XPS, questions often arise that deal with layers of the sample. For example, is the sample homogenous, with a consistent composition throughout, or layered, with certain elements or components residing in specific places in the sample? (Figure 1.70 b,c). A simple way to determine the answer to this question is to perform a depth analysis. By sputtering away the sample, data can be collected at different depths within the sample. It should be noted that sputtering is a destructive process. Within the XPS instrument, the sample is subjected to an Ar^+ ion beam that etches the surface. This creates a hole in the surface, allowing the X-rays to hit layers that would not have otherwise been analyzed. However, it should be realized that different surfaces and layers may be etched at different rates, meaning the same amount of etching does not occur during the same amount of time, depending on the element or compound currently being sputtered.

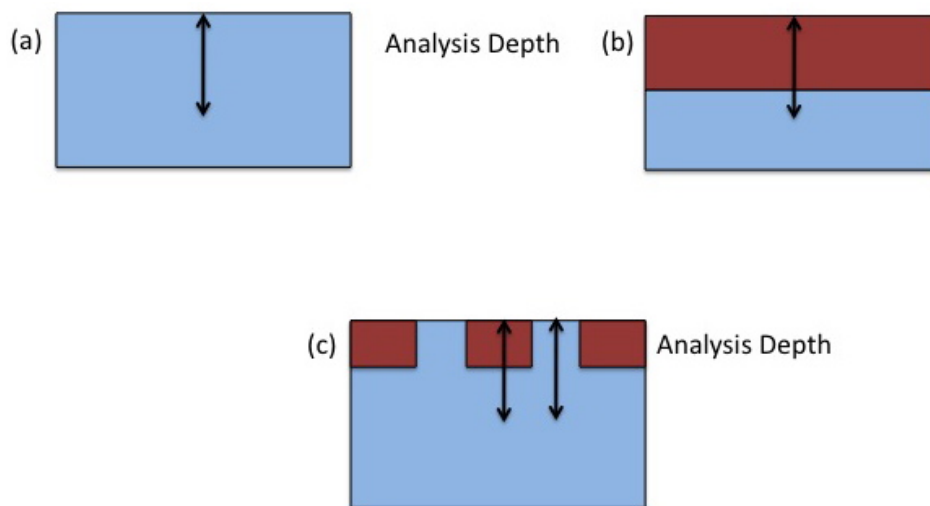


Figure 1.70: Schematic representation of analysis of (a) an homogeneous sample, as compared to (b) an homogeneous layers in a sample, and (c) an inhomogeneous layers in a sample.

It is important to note that hydrocarbons sputter very easily and can contaminate the high vacuum of the XPS instrument and thus later samples. They can also migrate to a recently sputtered (and hence unfunctionalized) surface after a short amount of time, so it is imperative to sputter and take a measurement quickly, otherwise the sputtering may appear to have had no effect.

1.8.1.2.2 Functionalized Films

When running XPS, it is important that the sample is prepared correctly. If it is not, there is a high chance of ruining not only data acquisition, but the instrument as well. With organic functionalization, it is very important to ensure the surface functional group (or as is the case with many functionalized nanoparticles, the surfactant) is immobile on the surface of the substrate. If it is removed easily in the vacuum chamber, it not only will give erroneous data, but it will contaminate the machine, which may then contaminate future samples. This is particularly important when studying thiol functionalization of gold samples, as thiol groups

bond strongly with the gold. If there is any loose thiol group contaminating the machine, the thiol will attach itself to any gold sample subsequently placed in the instrument, providing erroneous data. Fortunately, with the above exception, preparing samples that have been functionalized is not much different than standard preparation procedures. However, methods for analysis may have to be modified in order to obtain good, consistent data.

A common method for the analysis of surface modified material is angle resolved X-ray photoelectron spectroscopy (ARXPS). ARXPS is a non-destructive alternative to sputtering, as it relies upon using a series of small angles to analyze the top layer of the sample, giving a better picture of the surface than standard XPS. ARXPS allows for the analysis of the topmost layer of atoms to be analyzed, as opposed to standard XPS, which will analyze a few layers of atoms into the sample, as illustrated in Figure 1.71. ARXPS is often used to analyze surface contaminations, such as oxidation, and surface modification or passivation. Though the methodology and limitations are beyond the scope of this module, it is important to remember that, like normal XPS, ARXPS assumes homogeneous layers are present in samples, which can give erroneous data, should the layers be heterogeneous.

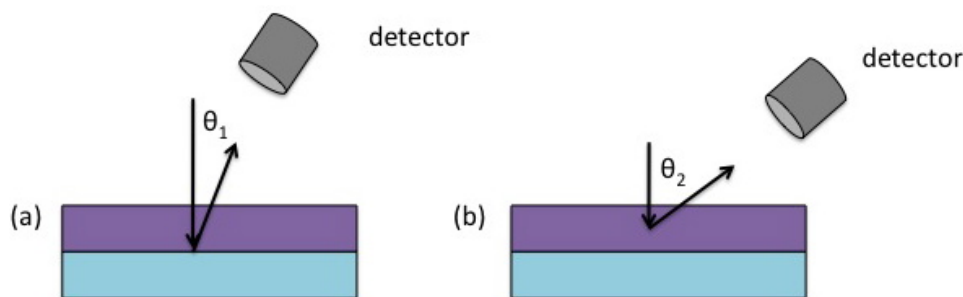


Figure 1.71: Schematic representation of (a) a standard XPS analysis and (b) ARXPS on a multilayer sample.

1.8.1.3 Limitations of XPS

There are many limitations to XPS that are not based on the samples or preparation, but on the machine itself. One such limitation is that XPS cannot detect hydrogen or helium. This, of course, leads to a ratio of elements in the sample that is not entirely accurate, as there is always some amount of hydrogen. It is a common fallacy to assume the percent of atoms obtained from XPS data are completely accurate due to this presence of undetected hydrogen (Table 1.8).

It is possible to indirectly measure the amount of hydrogen in a sample using XPS, but it is not very accurate and has to be done in a roundabout, often time consuming manner. If the sample contains hydrogen with a partial positive charge (i.e. OH), the sample can be washed in sodium naphthalenide ($C_{10}H_8Na$). This replaces this hydrogen with sodium, which can then be measured. The sodium to oxygen ratio that is obtained infers the hydrogen to oxygen ratio, assuming that all the hydrogen atoms have reacted.

XPS can only give an average measurement, as the electrons lower down in the sample will lose more energy as they pass other atoms while the electrons on the surface retain their original kinetic energy. The electrons from lower layers can also undergo inelastic or elastic scattering, seen in Figure 1.72. This scattering may have a significant impact on data at higher angles of emission. The beam itself is also relatively wide, with the smallest width ranging from 10 – 200 μm , lending to the observed average composition inside the

beam area. Due to this, XPS cannot differentiate sections of elements if the sections are smaller than the size of the beam.

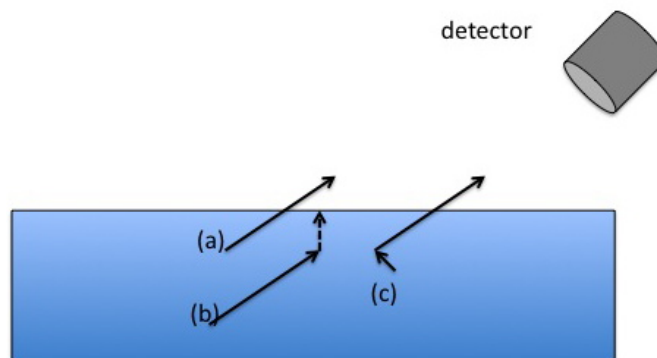


Figure 1.72: Schematic representation of (a) no scattering, (b) inelastic scattering, and (c) elastic scattering.

Sample reaction or degradation are important considerations. Caution should be exercised when analyzing polymers, as they are often chemically active and X-rays will provide energy to start degrading the polymer, altering the properties of the sample. One method found to help overcome this particular limitation is to use angle-resolved X-ray photoelectron spectroscopy (ARXPS). XPS can often reduce certain metal salts, such as Cu^{2+} . This reduction will give peaks that indicate a certain set of properties or chemical environments when it could be completely different. It needs to be understood that charges can build up on the surface of the sample due to a number of reasons, specifically due to the loss of electrons during the XPS experiment. The charge on the surface will interact with the electrons escaping from the sample, affecting the data obtained. If the charge collecting is positive, the electrons that have been knocked off will be attracted to the charge, slowing the electrons. The detector will pick up a lower kinetic energy of the electrons, and thus calculate a different binding energy than the one expected, giving peaks which could be labeled with an incorrect oxidation state or chemical environment. To overcome this, the spectra must be charge referenced by one of the following methods: using the naturally occurring graphite peak as a reference, sputtering with gold and using the gold peak as a reference or flooding the sample with the ion gun and waiting until the desired peak stops shifting.

1.8.1.3.1 Limitations with surfactants and sputtering

While it is known that sputtering is destructive, there are a few other limitations that are not often considered. As mentioned above, the beam of X-rays is relatively large, giving an average composition in the analysis. Sputtering has the same limitation. If the surfactant or layers are not homogeneous, then when the sputtering is finished and detection begins, the analysis will show a homogeneous section, due to the size of both the beam and sputtered area, while it is actually separate sections of elements.

The chemistry of the compounds can be changed with sputtering, as it removes atoms that were bonded, changing the oxidation state of a metal or the hybridization of a non-metal. It can also introduce charges if the sample is non-conducting or supported on a non-conducting surface.

1.8.1.4 Bibliography

- A. W. Apblett, A. C. Warren, and A. R. Barron, *Chem. Mater.*, 1992, **4**, 167.
- A. Herrera-Gomez, J. T. Grant, P. J. Cumpson, M. Jenko, F. S. Aguirre-Tostado, C. R. Brundle, T. Conrad, G. Conti, C. S. Fadley, J. Fulghum, K. Kobayashi, L. Kövér, H. Nohira, R. L. Opila, S. Oswald, R. W. Paynter, R. M. Wallace, W. S. M. Werner, and J. Wolstenhome. *Surf. Interface Anal.*, 2009, **41**, 840.
- C. C. Landry, J. A. Davis, A. W. Apblett, and A. R. Barron. *J. Mater. Chem.*, 1993, **3**, 597.
- S. F. Mao, Z. M. Zhang, K. Tokesi, A. Csik, J. Toth, R. J. Bereczky, and Z. J. Ding. *Surf. Interface Anal.*, 2008, **40**, 728.
- J. F. Moulden, W. F. Stickle, P. E. Sobol, and K. D. Bumben. *Handbook of X-ray Photoelectron Spectroscopy*, Physical Electronics Inc. (1995).
- J. P. Sibilía. *Materials Characterization and Chemical Analysis*, 2nd edn., Wiley-VCH (1996).

1.8.2 Using XPS to Analyze Metal Nanoparticles¹⁴

1.8.2.1 Introduction

X-ray photoelectron spectroscopy (XPS) is a surface technique developed for use with thin films. More recently, however, it has been used to analyze the chemical and elemental composition of nanoparticles. The complication of nanoparticles is that they are neither flat nor larger than the diameter of the beam, creating issues when using the data obtained at face value. Samples of nanoparticles will often be large aggregates of particles. This creates problems with the analysis acquisition, as there can be a variety of cross-sections, as seen in Figure 1.73. This acquisition problem is also compounded by the fact that the surfactant may not be completely covering the particle, as the curvature of the particle creates defects and divots. Even if it is possible to create a monolayer of particles on a support, other issues are still present. The background support will be analyzed with the particle, due to their small size and the size of the beam and the depth at which it can penetrate.

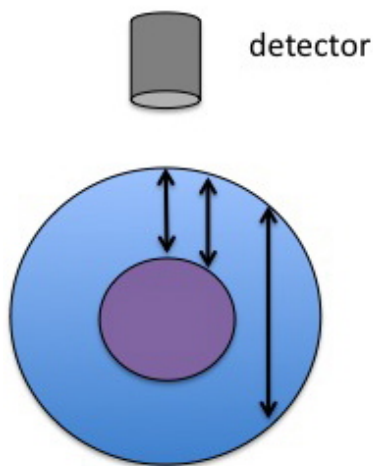


Figure 1.73: Different cross-sections of analysis possible on a nanoparticle.

¹⁴This content is available online at <<http://cnx.org/content/m34526/1.1/>>.

Many other factors can introduce changes in nanoparticles and their properties. There can be probe, environmental, proximity, and sample preparation effects. The dynamics of particles can wildly vary depending on the reactivity of the particle itself. Sputtering can also be a problem. The beam used to sputter will be roughly the same size or larger than the particles. This means that what appears in the data is not a section of particle, but an average composition of several particles.

Each of these issues needs to be taken into account and preventative measures need to be used so the data is the best representation possible.

1.8.2.2 Sample preparation

Sample preparation of nanoparticles is very important when using XPS. Certain particles, such as iron oxides without surfactants, will interact readily with oxygen in the air. This causes the particles to gain a layer of oxygen contamination. When the particles are then analyzed, oxygen appears where it should not and the oxidation state of the metal may be changed. As shown by these particles, which call for handling, mounting and analysis without exposure to air, knowing the reactivity of the nanoparticles in the sample is very important even before starting analysis. If the reactivity of the nanoparticle is known, such as the reactivity of oxygen and iron, then preventative steps can be taken in sample preparation in order to obtain the best analysis possible.

When preparing a sample for XPS, a powder form is often used. This preparation, however, will lead to aggregation of nanoparticles. If analysis is performed on such a sample, the data obtained will be an average of composition of each nanoparticle. If composition of a single particle is what is desired, then this average composition will not be sufficient. Fortunately, there are other methods of sample preparation. Samples can be supported on a substrate, which will allow for analysis of single particles. A pictorial representation in Figure 1.74 shows the different types of samples that can occur with nanoparticles.

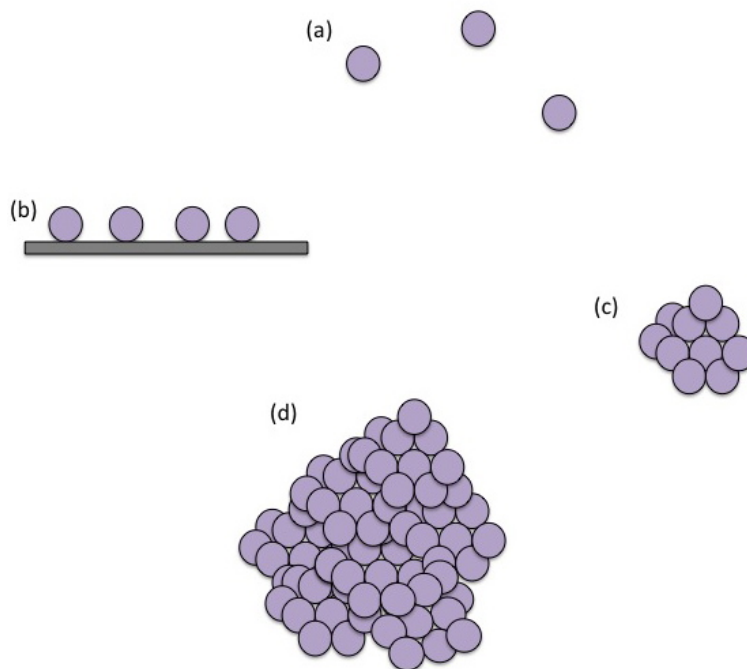


Figure 1.74: Representation of (a) a theoretical isolated nanoparticles, (b) nanoparticles suspended on a substrate, (c) an aggregate of nanoparticles, and (d) a powdered form of nanoparticles.

1.8.2.3 Analysis limitations

Nanoparticles are dynamic; their properties can change when exposed to new chemical environments, leading to a new set of applications. It is the dynamics of nanoparticles that makes them so useful and is one of the reasons why scientists strive to understand their properties. However, it is this dynamic ability that makes analysis difficult to do properly. Nanoparticles are easily damaged and can change properties over time or with exposure to air, light or any other environment, chemical or otherwise. Surface analysis is often difficult because of the high rate of contamination. Once the particles are inserted into XPS, even more limitations appear.

1.8.2.3.1 Probe effects

There are often artifacts introduced from the simple mechanism of conducting the analysis. When XPS is used to analyze the relatively large surface of thin films, there is small change in temperature as energy is transferred. The thin films, however, are large enough that this small change in energy has to significant change to its properties. A nanoparticle is much smaller. Even a small amount of energy can drastically change the shape of particles, in turn changing the properties, giving a much different set of data than expected.

The electron beam itself can affect how the particles are supported on a substrate. Theoretically, nanoparticles would be considered separate from each other and any other chemical environments, such as solvents or substrates. This, however, is not possible, as the particles must be suspended in a solution or placed on a

substrate when attempting analysis. The chemical environment around the particle will have some amount of interaction with the particle. This interaction will change characteristics of the nanoparticles, such as oxidation states or partial charges, which will then shift the peaks observed. If particles can be separated and suspended on a substrate, the supporting material will also be analyzed due to the fact that the X-ray beam is larger than the size of each individual particle. If the substrate is made of porous materials, it can adsorb gases and those will be detected along with the substrate and the particle, giving erroneous data.

1.8.2.3.2 Environmental effects

Nanoparticles will often react, or at least interact, with their environments. If the particles are highly reactive, there will often be induced charges in the near environment of the particle. Gold nanoparticles have a well-documented ability to undergo plasmon interactions with each other. When XPS is performed on these particles, the charges will change the kinetic energy of the electrons, shifting the apparent binding energy. When working with nanoparticles that are well known for creating charges, it is often best to use an ion gun or a coating of gold. The purpose of the ion gun or gold coating is to try to move peaks back to their appropriate energies. If the peaks do not move, then the chance of there being no induced charge is high and thus the obtained data is fairly reliable.

1.8.2.3.3 Proximity effects

The proximity of the particles to each other will cause interactions between the particles. If there is a charge accumulation near one particle, and that particle is in close proximity with other particles, the charge will become enhanced as it spreads, affecting the signal strength and the binding energies of the electrons. While the knowledge of charge enhancement could be useful to potential applications, it is not beneficial if knowledge of the various properties of individual particles is sought.

Less isolated (i.e., less crowded) particles will have different properties as compared to more isolated particles. A good example of this is the plasmon effect in gold nanoparticles. The closer gold nanoparticles are to each other, the more likely they will induce the plasmon effect. This can change the properties of the particles, such as oxidation states and partial charges. These changes will then shift peaks seen in XPS spectra. These proximity effects are often introduced in the sample preparation. This, of course, shows why it is important to prepare samples correctly to get desired results.

1.8.2.4 Conclusions

Unfortunately there is no good general procedure for all nanoparticles samples. There are too many variables within each sample to create a basic procedure. A scientist wanting to use XPS to analyze nanoparticles must first understand the drawbacks and limitations of using their sample as well as how to counteract the artifacts that will be introduced in order to properly use XPS.

One must never make the assumption that nanoparticles are flat. This assumption will only lead to a misrepresentation of the particles. Once the curvature and stacking of the particles, as well as their interactions with each other are taken into account, XPS can be run.

1.8.2.5 Bibliography

- D. R. Baer and M. H. Engelhard. *J. Electron Spectrosc. Rel. Phenom.*, 2009, **178-179**, 415.
- D. R. Baer, J. E. Amonette, M. H. Engelhard, D. J. Gaspar, A. S. Karakoti, S. Kuchibhatla, P. Nachimuthu, J. T. Nurmi, Y. Qiang, V. Sarathy, S. Seal, A. Sharma. P. G. Tratnyek, and C. M. Wang. *Surf. Interface Anal.*, 2008, **40**, 529.

1.9 Auger Electron Spectroscopy ¹⁵

1.9.1 Basic principles

Auger electron spectroscopy (AES) is one of the most commonly employed surface analysis techniques. It uses the energy of emitted electrons to identify the elements present in a sample, similar to X-ray photoelectron spectroscopy (XPS). The main difference is that XPS uses an X-ray beam to eject an electron while AES uses an electron beam to eject an electron. In AES, the sample depth is dependent on the escape energy of the electrons. It is not a function of the excitation source as in XPS. In AES, the collection depth is limited to 1-5 nm due to the small escape depth of electrons, which permits analysis of the first 2 - 10 atomic layers. In addition, a typical analysis spot size is roughly 10 nm. A representative AES spectrum illustrating the number of emitted electrons, N , as a function of kinetic energy, E , in direct form (red) and in differentiated form (black) is shown in Figure 1.75.

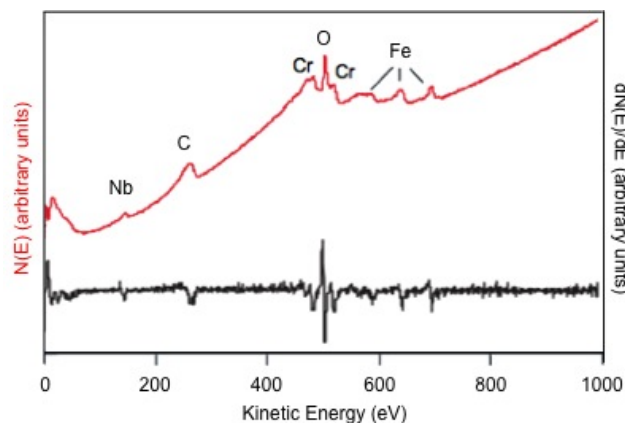


Figure 1.75: AES survey spectrum (red) and differentiated spectrum (black) of an oxidized Fe-Cr-Nb alloy. Adapted from H. J. Mathieu in *Surface Analysis: The Principal Techniques*, 2nd Edition, Ed. J. C. Vickerman, Wiley-VCH, Weinheim (2011).

Like XPS, AES measures the kinetic energy (E_k) of an electron to determine its binding energy (E_b). The binding energy is inversely proportional to the kinetic energy and can be found from (1.57), where $h\nu$ is the energy of the incident photon and $\Delta\Phi$ is the difference in work function between the sample and the detector material.

$$E_b = h\nu - E_k + \Delta\Phi \quad (1.57)$$

Since the E_b is dependent on the element and the electronic environment of the nucleus, AES can be used to distinguish elements and their oxidation states. For instance, the energy required to remove an electron from Fe^{3+} is more than in Fe^0 . Therefore, the Fe^{3+} peak will have a lower E_k than the Fe^0 peak, effectively distinguishing the oxidation states.

¹⁵This content is available online at <<http://cnx.org/content/m43546/1.1/>>.

1.9.2 Auger process

An Auger electron comes from a cascade of events. First, an electron beam comes in with sufficient energy to eject a core electron creating a vacancy (see Figure 1.76A). Typical energies of the primary electrons range from 3 - 30 keV. A secondary electron (imaging electron) of higher energy drops down to fill the vacancy (see Figure 1.76B) and emits sufficient energy to eject a tertiary electron (Auger electron) from a higher shell (see Figure 1.76C).

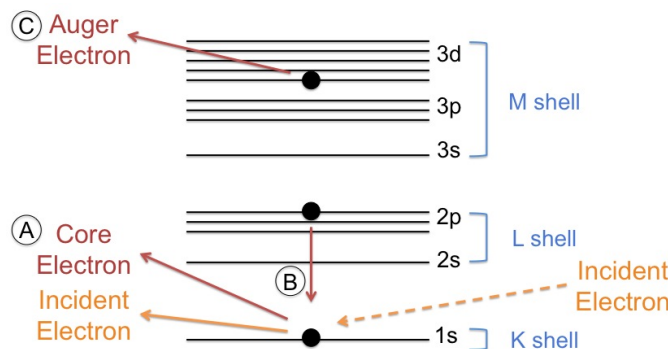


Figure 1.76: Schematic diagram of the Auger process.

The shells from which the electrons move from lowest to highest energy are described as the K shell, L shell, and M shell. This nomenclature is related to quantum numbers. Explicitly, the K shell represents the 1s orbital, the L shell represents the 2s and 2p orbitals, and the M shell represents the 3s, 3p, and 3d orbitals. The cascade of events typically begins with the ionization of a K shell electron, followed by the movement of an L shell electron into the K shell vacancy. Then, either an L shell electron or M shell electron is ejected. It depends on the element, which peak is prevalent but often both peaks will be present. The peak seen in the spectrum is labeled according to the shells involved in the movement of the electrons. For example, an electron ejected from a gold atom could be labeled as Au KLL or Au KLM.

The intensity of the peak depends on the amount of material present, while the peak position is element dependent. Auger transitions characteristic of each elements can be found in the literature. Auger transitions of the first forty detectable elements are listed in Table 1.10.

Atomic number	Element	AES transition	Kinetic energy of transition (eV)
3	Li	KLL	43
4	Be	KLL	104
<i>continued on next page</i>			

5	B	KLL	179
6	C	KLL	272
7	N	KLL	379
8	O	KLL	508
9	F	KLL	647
11	Na	KLL	990
12	Mg	KLL	1186
13	Al	LMM	68
14	Si	LMM	92
15	P	LMM	120
16	S	LMM	152
17	Cl	LMM	181
19	K	KLL	252
20	Ca	LMM	291
21	Sc	LMM	340
22	Ti	LMM	418
23	V	LMM	473
24	Cr	LMM	529
25	Mn	LMM	589
26	Fe	LMM	703
27	Co	LMM	775
28	Ni	LMM	848
29	Cu	LMM	920
30	Zn	LMM	994
31	Ga	LMM	1070
32	Ge	LMM	1147
33	As	LMM	1228
34	Se	LMM	1315
<i>continued on next page</i>			

35	Br	LMM	1376
39	Y	MNN	127
40	Zr	MNN	147
41	Nb	MNN	167
42	Mo	MNN	186

Table 1.10: Selected AES transitions and their corresponding kinetic energy. Adapted from H. J. Mathieu in *Surface Analysis: The Principal Techniques*, Second Edition, Ed. J. C. Vickerman, Wiley-VCH, Weinheim (2011).

1.9.3 Instrumentation

Important elements of an Auger spectrometer include a vacuum system, an electron source, and a detector. AES must be performed at pressures less than 10^{-3} pascal (Pa) to keep residual gases from adsorbing to the sample surface. This can be achieved using an ultra-high-vacuum system with pressures from 10^{-8} to 10^{-9} Pa. Typical electron sources include tungsten filaments with an electron beam diameter of 3 - 5 μm , LaB_6 electron sources with a beam diameter of less than 40 nm, and Schottky barrier filaments with a 20 nm beam diameter and high beam current density. Two common detectors are the cylindrical mirror analyzer and the concentric hemispherical analyzer discussed below. Notably, concentric hemispherical analyzers typically have better energy resolution.

1.9.3.1 Cylindrical mirror analyzer (CMA)

A CMA is composed of an electron gun, two cylinders, and an electron detector (Figure 1.77). The operation of a CMA involves an electron gun being directed at the sample. An ejected electron then enters the space between the inner and outer cylinders (IC and OC). The inner cylinder is at ground potential, while the outer cylinder's potential is proportional to the kinetic energy of the electron. Due to its negative potential, the outer cylinder deflects the electron towards the electron detector. Only electrons within the solid angle cone are detected. The resulting signal is proportional to the number of electrons detected as a function of kinetic energy.

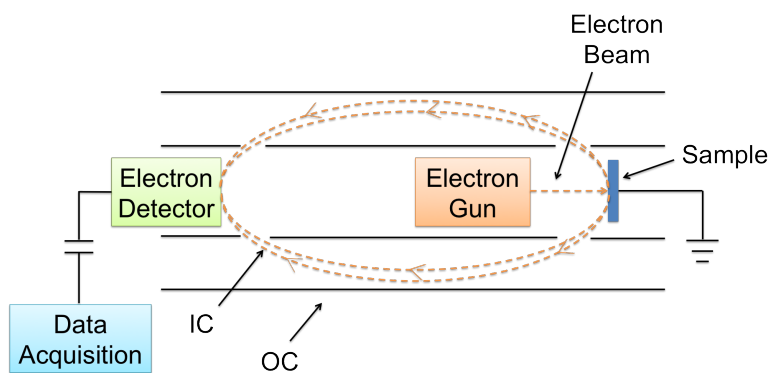


Figure 1.77: Schematic of a cylindrical mirror analyzer.

1.9.3.2 Concentric hemispherical analyzer (CHA)

A CHA contains three parts (Figure 1.78):

1. A retarding and focusing input lens assembly.
2. An inner and outer hemisphere (IH and OH).
3. An electron detector.

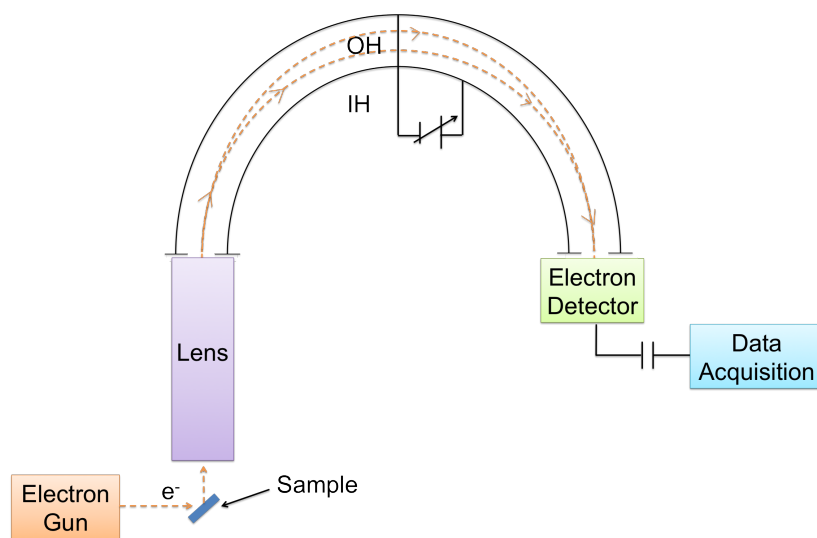


Figure 1.78: Schematic of a concentric hemispherical analyzer.

Electrons ejected from the surface enter the input lens, which focuses the electrons and retards their energy for better resolution. Electrons then enter the hemispheres through an entrance slit. A potential difference is applied on the hemispheres so that only electrons with a small range of energy differences reach the exit. Finally, an electron detector analyzes the electrons.

1.9.4 Applications

AES has widespread use owing to its ability to analyze small spot sizes with diameters from 5 μm down to 10 nm depending on the electron gun. For instance, AES is commonly employed to study film growth and surface-chemical composition, as well as grain boundaries in metals and ceramics. It is also used for quality control surface analyses in integrated circuit production lines due to short acquisition times. Moreover, AES is used for areas that require high spatial resolution, which XPS cannot achieve. AES can also be used in conjunction with transmission electron microscopy (TEM) and scanning electron microscopy (SEM) to obtain a comprehensive understanding of microscale materials, both chemically and structurally. As an example of combining techniques to investigate microscale materials, Figure 1.79 shows the characterization of a single wire from a Sn-Nb multi-wire alloy. Figure 1.79a is a SEM image of the singular wire and Figure 1.79b is a schematic depicting the distribution of Nb and Sn within the wire. Point analysis was performed along the length of the wire to determine the percent concentrations of Nb and Sn.

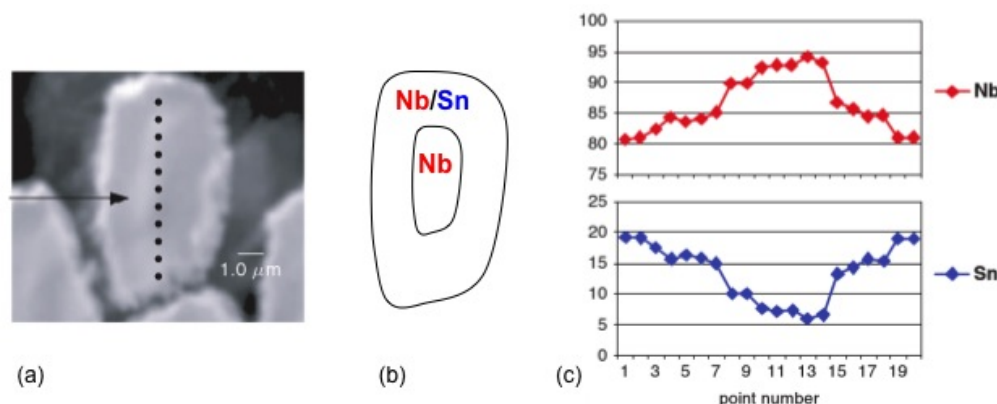


Figure 1.79: Analysis of a Sn-Nb wire. (a) SEM image of the wire, (b) schematic of the elemental distribution, and (c) graphical representation of point analysis giving the percent concentration of Nb and Sn. Adapted from H. J. Mathieu in *Surface Analysis: The Principal Techniques*, Second Edition, Ed. J. C. Vickerman, Wiley-VCH, Weinheim (2011).

AES is widely used for depth profiling. Depth profiling allows the elemental distributions of layered samples 0.2 – 1 μm thick to be characterized beyond the escape depth limit of an electron. Varying the incident and collection angles, and the primary beam energy controls the analysis depth. In general, the depth resolution decreases with the square root of the sample thickness. Notably, in AES, it is possible to simultaneously sputter and collect Auger data for depth profiling. The sputtering time indicates the depth and the intensity indicates elemental concentrations. Since, the sputtering process does not affect the ejection of the Auger electron, helium or argon ions can be used to sputter the surface and create the trench, while collecting Auger data at the same time. The depth profile does not have the problem of diffusion of hydrocarbons into the trenches. Thus, AES is better for depth profiles of reactive metals (e.g., gold or any metal or semiconductor). Yet, care should be taken because sputtering can mix up different elements, changing the sample composition.

1.9.5 Limitations

While AES is a very valuable surface analysis technique, there are limitations. Because AES is a three-electron process, elements with less than three electrons cannot be analyzed. Therefore, hydrogen and helium cannot be detected. Nonetheless, detection is better for lighter elements with fewer transitions. The numerous transition peaks in heavier elements can cause peak overlap, as can the increased peak width of higher energy transitions. Detection limits of AES include 0.1 – 1% of a monolayer, 10^{-16} – 10^{-15} g of material, and 10^{12} – 10^{13} atoms/cm².

Another limitation is sample destruction. Although focusing of the electron beam can improve resolution; the high-energy electrons can destroy the sample. To limit destruction, beam current densities of greater than 1 mA/cm² should be used. Furthermore, charging of the electron beam on insulating samples can deteriorate the sample and result in high-energy peak shifts or the appearance of large peaks.

1.9.6 Bibliography

- H. Bubert, J. Rivière, and W. Werner, *Surface and Thin Film Analysis: A Compendium of Principles, Instrumentation, and Applications*, Second Edition, Ed. G. Friedbacher and H. Bubert, Wiley-VCH,

Weinheim (2011).

- H. Lüth in *Solid Surfaces, Interfaces and Thin Films*, Fifth Edition, Springer, New York (2010).
- H. J. Mathieu in *Surface Analysis: The Principal Techniques*, Second Edition, Ed. J. C. Vickerman, Wiley-VCH, Weinheim (2011).
- S. N. Raman, D. F. Paul, J. S. Hammond, and K. D. Bomben, *Microscopy Today*, 2011, **19**, 12.
- N. Turner in *Analytical Instrumentation Handbook*, Second Edition, Ed. G. Ewing, Marcel Dekker, Inc, New York (1997).
- J. F. Watts in *Handbook of Adhesion Technology*, Ed. Lucas F.M. da Silva, A. Öchsner, and R. Adams, Springer, New York (2011).
- V. Young and G. Hoflund in *Handbook of Surface and Interface Analysis Methods for Problem-Solving*, Second Edition, Ed. J. Rivière and S. Myhra, CRC Press, Boca Raton (2009).

1.10 An Introduction to Energy Dispersive X-ray Spectroscopy ¹⁶

1.10.1 Introduction

Energy-dispersive X-ray spectroscopy (EDX or EDS) is an analytical technique used to probe the composition of a solid materials. Several variants exist, but the all rely on exciting electrons near the nucleus, causing more distant electrons to drop energy levels to fill the resulting “holes.” Each element emits a different set of X-ray frequencies as their vacated lower energy states are refilled, so measuring these emissions can provide both qualitative and quantitative information about the near-surface makeup of the sample. However, accurate interpretation of this data is dependent on the presence of high-quality standards, and technical limitations can compromise the resolution.

1.10.2 Physical underpinnings

In the quantum mechanical model of the atom, an electron’s energy state is defined by a set of quantum numbers. The primary quantum number, n , provides the coarsest description of the electron’s energy level, and all the sublevels that share the same primary quantum number are sometimes said to comprise an energy “shell.” Instead of describing the lowest-energy shell as the “ $n = 1$ shell,” it is more common in spectroscopy to use alphabetical labels: The K shell has $n = 1$, the L shell has $n = 2$, the M shell has $n = 3$, and so on. Subsequent quantum numbers divide the shells into subshells: one for K, three for L, and five for M. Increasing primary quantum numbers correspond with increasing average distance from the nucleus and increasing energy (Figure 1.80). An atom’s core shells are those with lower primary quantum numbers than the highest occupied shell, or valence shell.

¹⁶This content is available online at <<http://cnx.org/content/m43555/1.1/>>.

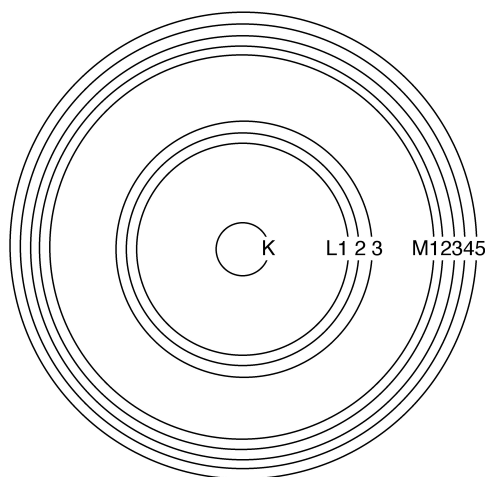


Figure 1.80: A diagram of the core electronic energy levels of an atom, with the lowest energy shell, K, nearest the nucleus. Circles are used here for convenience – they are not meant to represent the shapes of the electron's orbitals. Adapted from *Introduction to Energy Dispersive X-ray Spectroscopy (EDS)* , <http://micron.ucr.edu/public/manuals/EDS-intro.pdf> ¹⁷.

Transitions between energy levels follow the law of conservation of energy. Excitation of an electron to a higher energy state requires an input of energy from the surroundings, and relaxation to a lower energy state releases energy to the surroundings. One of the most common and useful ways energy can be transferred into and out of an atom is by electromagnetic radiation. Core shell transitions correspond to radiation in the X-ray portion of the spectrum; however, because the core shells are normally full by definition, these transitions are not usually observed.

X-ray spectroscopy uses a beam of electrons or high-energy radiation (see instrument variations, below) to excite core electrons to high energy states, creating a low-energy vacancy in the atoms' electronic structures. This leads to a cascade of electrons from higher energy levels until the atom regains a minimum-energy state. Due to conservation of energy, the electrons emit X-rays as they transition to lower energy states. It is these X-rays that are being measured in X-ray spectroscopy. The energy transitions are named using the letter of the shell where ionization first occurred, a Greek letter denoting the group of lines that transition belongs to, in order of decreasing importance, and a numeric subscript ranking the peak's intensity within that group. Thus, the most intense peak resulting from ionization in the K shell would be $K\alpha_1$ (Figure 1.81). Since each element has a different nuclear charge, the energies of the core shells and, more importantly, the spacing between them vary from one element to the next. While not every peak in an element's spectrum is exclusive to that element, there are enough characteristic peaks to be able to determine composition of the sample, given sufficient resolving power.

¹⁷<http://micron.ucr.edu/public/manuals/EDS-intro.pdf>

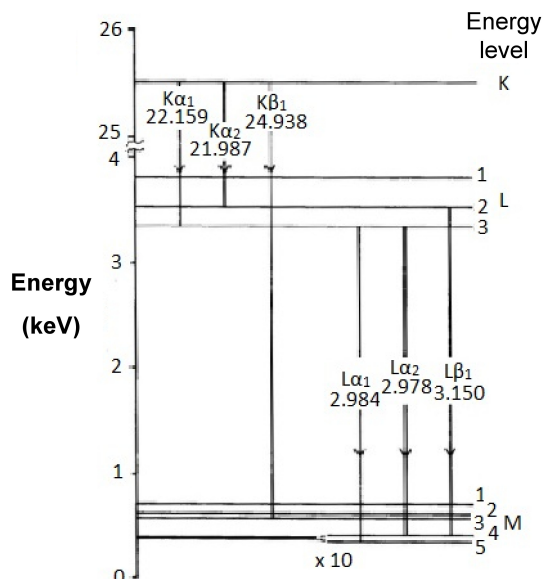


Figure 1.81: A diagram of the energy transitions after the excitation of a gold atom. The arrows show the direction the vacancy moves when the higher energy electrons move down to refill the core. Adapted from *Introduction to Energy Dispersive X-ray Spectroscopy (EDS)*, <http://micron.ucr.edu/public/manuals/EDS-intro.pdf> ¹⁸.

1.10.3 Instrumentation and sample preparation

1.10.3.1 Instrument variations

There are two common methods for exciting the core electrons off the surface atoms. The first is to use a high-energy electron beam like the one in a scanning electron microscope (SEM). The beam is produced by an electron gun, in which electrons emitted thermionically from a hot cathode are guided down the column by an electric field and focused by a series of negatively charged “lenses.” X-rays emitted by the sample strike a lithium-drifted silicon *p-i-n* junction plate. This promotes electrons in the plate into the conduction band, inducing a voltage proportional to the energy of the impacting X-ray which generally falls between about 1 and 10 keV. The detector is cooled to liquid nitrogen temperatures to reduce electronic noise from thermal excitations.

It is also possible to use X-rays to excite the core electrons to the point of ionization. In this variation, known as energy-dispersive X-ray fluorescence analysis (EDXRFA or XRF), the electron column is replaced by an X-ray tube and the X-rays emitted by the sample in response to the bombardment are called secondary X-rays, but these variants are otherwise identical.

Regardless of the excitation method, subsequent interactions between the emitted X-rays and the sample can lead to poor resolution in the X-ray spectrum, producing a Gaussian-like curve instead of a sharp peak. Indeed, this spreading of energy within the sample combined with the penetration of the electron or X-ray beam leads to the analysis of a roughly $1 \mu\text{m}^3$ volume instead of only the surface features. Peak broadening can lead to overlapping peaks and a generally misleading spectrum. In cases where a normal EDS spectrum

¹⁸<http://micron.ucr.edu/public/manuals/EDS-intro.pdf>

is inadequately resolved, a technique called wavelength-dispersive X-ray spectroscopy (WDS) can be used. The required instrument is very similar to the ones discussed above, and can use either excitation method. The major difference is that instead of having the X-rays emitted by the sample hit the detector directly, they first encounter an analytical crystal of known lattice dimensions. Bragg's law predicts that the strongest reflections off the crystal will occur for wavelengths such that the path difference between rays reflecting from consecutive layers in the lattice is equal to an integral number of wavelengths. This is represented mathematically as (1.58), where n is an integer, λ is the wavelength of impinging light, d is the distance between layers in the lattice, and θ is the angle of incidence. The relevant variables for the equation are labeled in Figure 1.82.

$$n\lambda = 2d \sin\theta \quad (1.58)$$

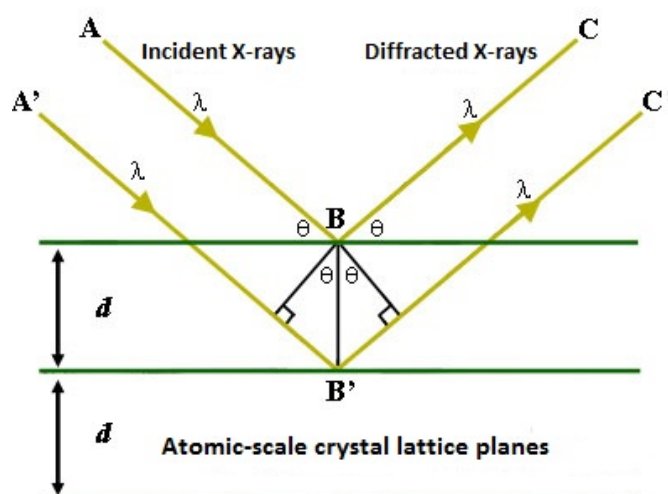


Figure 1.82: A diagram of a light beam impinging on a crystal lattice. If the light meets the criterion $n\lambda = 2d \sin(\theta)$, Bragg's law predicts that the waves reflecting off each layer of the lattice interfere constructively, leading to a strong signal. Adapted from D. Henry, N. Eby, J. Goodge, and D. Mogk, *X-ray Reflection in Accordance with Bragg's Law*, http://serc.carleton.edu/research_education/geochemsheets/BraggsLaw.html ¹⁹.

By moving the crystal and the detector around the Rowland circle, the spectrometer can be tuned to examine specific wavelengths (Figure 1.83). Generally, an initial scan across all wavelengths is taken first, and then the instrument is programmed to more closely examine the wavelengths that produced strong peaks. The resolution available with WDS is about an order of magnitude better than with EDS because the analytical crystal helps filter out the noise of subsequent, non-characteristic interactions. For clarity, "X-ray spectroscopy" will be used to refer to all of the technical variants just discussed, and points made about EDS will hold true for XRF unless otherwise noted.

¹⁹http://serc.carleton.edu/research_education/geochemsheets/BraggsLaw.html

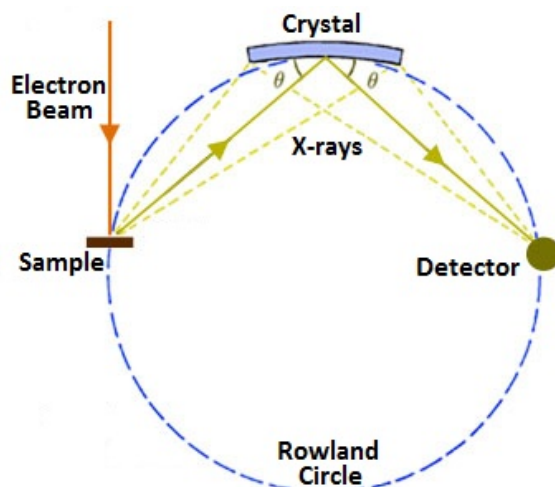


Figure 1.83: A schematic of a typical WDS instrument. The analytical crystal and the detector can be moved around an arc known as the Rowland Circle. This grants the operator the ability to change the angle between the sample, the crystal, and the detector, thereby changing the X-ray wavelength that would satisfy Bragg's law. The sample holder is typically stationary. Adapted from D. Henry and J. Goodge, *Wavelength-Dispersive X-ray Spectroscopy (WDS)* , http://serc.carleton.edu/research_education/geochemsheets/wds.html ²⁰.

1.10.3.2 Sample preparation

Compared with some analytical techniques, the sample preparation required for X-ray spectroscopy or any of the related methods just discussed is trivial. The sample must be stable under vacuum, since the sample chamber is evacuated to prevent the atmosphere from interfering with the electron beam or X-rays. It is also advisable to have the surface as clean as possible; X-ray spectroscopy is a near-surface technique, so it should analyze the desired material for the most part regardless, but any grime on the surface will throw off the composition calculations. Simple qualitative readings can be obtained from a solid of any thickness, as long as it fits in the machine, but for reliable quantitative measurements, the sample should be shaved as thin as possible.

1.10.4 Data interpretation

Qualitative analysis, the determination of which elements are present in the sample but not necessarily the stoichiometry, relies on empirical standards. The energies of the commonly used core shell transitions have been tabulated for all the natural elements. Since combinations of elements can act differently than a single element alone, standards with compositions as similar as possible to the suspected makeup of the sample are also employed. To determine the sample's composition, the peaks in the spectrum are matched with peaks from the literature or standards.

Quantitative analysis, the determination of the sample's stoichiometry, needs high resolution to be good enough that the ratio of the number of counts at each characteristic frequency gives the ratio of those elements in the sample. It takes about 40,000 counts for the spectrum to attain a 2σ precision of $\pm 1\%$. It is important

²⁰http://serc.carleton.edu/research_education/geochemsheets/wds.html

to note, however, that this is not necessarily the same as the empirical formula, since not all elements are visible. Spectrometers with a beryllium window between the sample and the detector typically cannot detect anything lighter than sodium. Spectrometers equipped with polymer based windows can quantify elements heavier than beryllium. Either way, hydrogen cannot be observed by X-ray spectroscopy.

X-ray spectra are presented with energy in keV on the x-axis and the number of counts on the y-axis. The EDX spectra of biotite and NIST glass K309 are shown as examples (Figure 1.84 and Figure 1.85, respectively). Biotite is a mineral similar to mica which has the approximate chemical formula $K(Mg,Fe)_3AlSi_3O_{10}(F,OH)_2$. Strong peaks for manganese, aluminum, silicon, potassium, and iron can be seen in the spectrum. The lack of visible hydrogen is expected, and the absence of oxygen and fluorine peaks suggests the instrument had a beryllium window. The titanium peak is small and unexpected, so it may only be present in trace amounts. K309 is a mix of glass developed by the National Institute for Standards and Technology. The spectrum shows that it contains significant amounts of silicon, aluminum, calcium, oxygen, iron, and barium. The large peak at the far left is the carbon signal from the carbon substrate the glass was placed on.

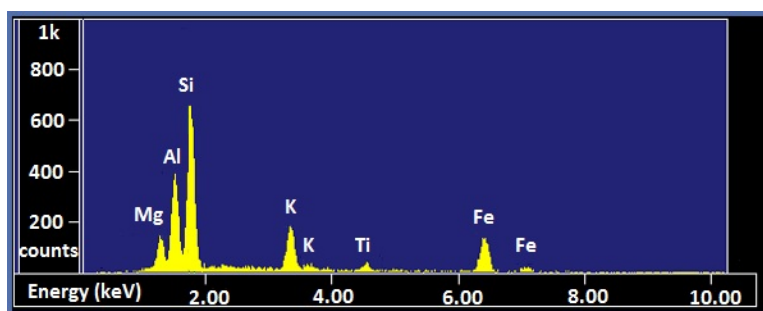


Figure 1.84: EDS spectrum of biotite. Silicon, aluminum, manganese, potassium, magnesium, iron, and titanium are all identifiable, though titanium appears to be only a trace component. Adapted from J. Goodge, *Energy-Dispersive X-ray Spectroscopy (EDS)*, http://serc.carleton.edu/research_education/geochemsheets/eds.html ²¹.

²¹http://serc.carleton.edu/research_education/geochemsheets/eds.html

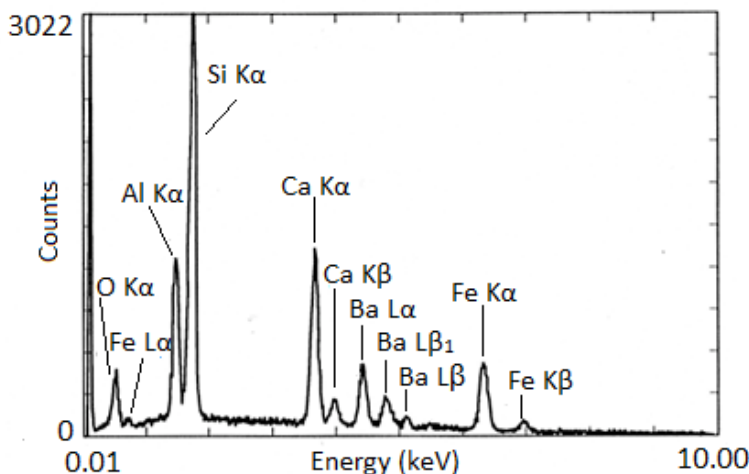


Figure 1.85: EDS spectrum of NIST K309 glass. Silicon, aluminum, barium, calcium, iron, and oxygen are identifiable in the spectrum. Adapted from J. Goldstein, D. Newbury, D. Joy, C. Lyman, P. Echlin, E. Lifshin, L. Sawyer, and J. Michael, *Scanning Electron Microscopy and X-ray Microanalysis*, 3rd, Springer, New York (2003).

1.10.5 Limitations

As has just been discussed, X-ray spectroscopy is incapable of seeing elements lighter than boron. This is a problem given the abundance of hydrogen in natural and man-made materials. The related techniques X-ray photoelectron spectroscopy (XPS) and Auger spectroscopy are able to detect Li and Be, but are likewise unable to measure hydrogen.

X-ray spectroscopy relies heavily on standards for peak identification. Because a combination of elements can have noticeably different properties from the individual constituent elements in terms of X-ray fluorescence or absorption, it is important to use a standard as compositionally similar to the sample as possible. Naturally, this is more difficult to accomplish when examining new materials, and there is always a risk of the structure of the sample being appreciably different than expected.

The energy-dispersive variants of X-ray spectroscopy sometimes have a hard time distinguishing between emissions that are very near each other in energy or distinguishing peaks from trace elements from background noise. Fortunately, the wavelength-dispersive variants are much better at both of these. The rough, stepwise curve in Figure 1.86 represents the EDS spectrum of molybdenite, a mineral with the chemical formula MoS_2 . Broadened peaks make it difficult to distinguish the molybdenum signals from the sulfur ones. Because WDS can select specific wavelengths, it has much better resolution and can pinpoint the separate peaks more accurately. Similarly, the trace silicon signal in the EDS spectrum of the nickel-aluminum-manganese alloy in Figure 1.87A is barely distinguishable as a bump in the baseline, but the WDS spectrum in Figure 1.87B clearly picks it up.

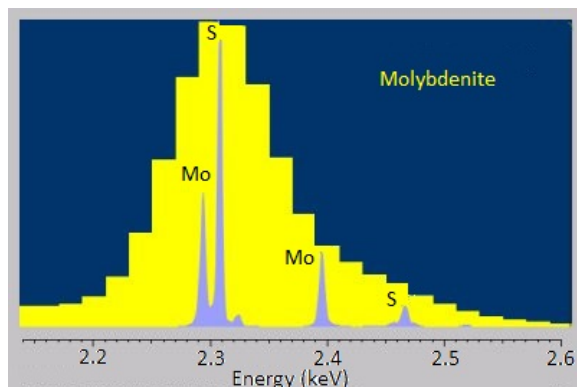


Figure 1.86: A comparison of the EDS (yellow) and WDS spectra (light blue) of a sample of molybdenite. The sulfur and molybdenum peaks are unresolved in the EDS spectrum, but are sharp and distinct in the WDS spectrum. Adapted from Oxford Instruments, *The power of WDS sensitivity and resolution*, <http://www.x-raymicroanalysis.com/x-ray-microanalysis-explained/pages/detectors/wave1.htm>²².

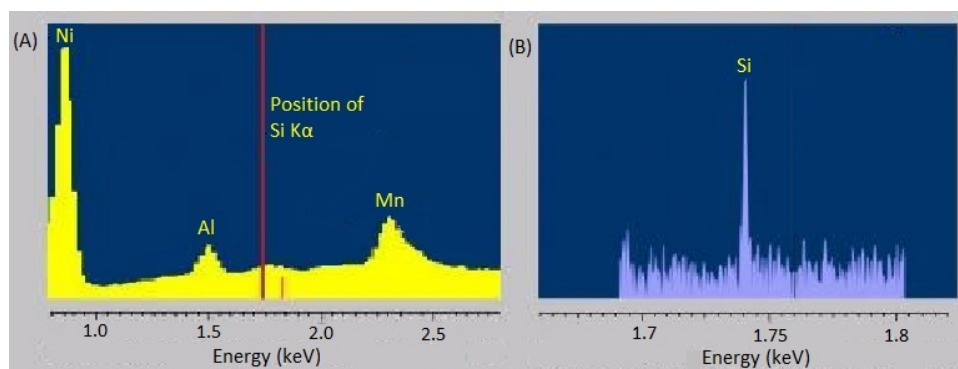


Figure 1.87: (A) The EDS spectrum of an alloy comprised primarily of sodium, aluminum, and manganese. Silicon is a trace element in the alloy, but is not discernible in the spectrum. (B) The WDS spectrum of the same alloy in the region around the characteristic silicon peak. In this measurement, the silicon emission stands out quite clearly. Adapted from Oxford Instruments, *The power of WDS sensitivity and resolution*, <http://www.x-raymicroanalysis.com/x-ray-microanalysis-explained/pages/detectors/wave1.htm>²³.

1.10.6 Bibliography

- N. A. Baily and G. Kramer, *Radiat. Res.*, 1964, **22**, 53.

²²<http://www.x-raymicroanalysis.com/x-ray-microanalysis-explained/pages/detectors/wave1.htm>

²³<http://www.x-raymicroanalysis.com/x-ray-microanalysis-explained/pages/detectors/wave1.htm>

- J. Goldstein, D. Newbury, D. Joy, C. Lyman, P. Echlin, E. Lifshin, L. Sawyer, and J. Michael, *Scanning Electron Microscopy and X-ray Microanalysis*, 3rd, Springer, New York (2003).
- J. Goodge, *Energy-Dispersive X-ray Spectroscopy (EDS)*, http://serc.carleton.edu/research_education/geochemsheets/.
- K. F. J. Heinrich, *Electron Beam Microanalysis*, Van Nostrand Reinhold, New York (1981).
- D. Henry and J. Goodge, *Wavelength-Dispersive X-ray Spectroscopy (WDS)*, http://serc.carleton.edu/research_education/geochemsheets/wds.html²⁵.
- D. Henry, N. Eby, J. Goodge, and D. Mogk, *X-ray Reflection in Accordance with Bragg's Law*, http://serc.carleton.edu/research_education/geochemsheets/BraggsLaw.html²⁶.
- Oxford Instruments, *The power of WDS sensitivity and resolution*, <http://www.x-raymicroanalysis.com/x-ray-microanalysis-explained/pages/detectors/wave1.htm>²⁷.
- C. Whiston, *X-ray Methods*, Published on behalf of ACOI, Thames Polytechnic, London, by Wiley, New York (1987).
- S. Zhang, L. Li, and A. Kumar, *Materials Characterisation Techniques*, CRC, Boca Raton (2009).
- *Introduction to Energy Dispersive X-ray Spectroscopy (EDS)*, <http://micron.ucr.edu/public/manuals/EDS-intro.pdf>²⁸.

1.11 Rutherford Backscattering of Thin Films ²⁹

1.11.1 Introduction

One of the main research interests of the semiconductor industry is to improve the performance of semi-conducting devices and to construct new materials with reduced size or thickness that have potential application in transistors and microelectronic devices. However, the most significant challenge regarding thin film semiconductor materials is measurement. Properties such as the thickness, composition at the surface, and contamination, all are critical parameters of the thin films. To address these issues, we need an analytical technique which can measure accurately through the depth of the of the semiconductor surface without destruction of the material. Rutherford backscattering spectroscopy is a unique analysis method for this purpose. It can give us information regarding in-depth profiling in a non-destructive manner. However X-ray photo electron spectroscopy (XPS), energy dispersive X-ray analysis (EDX) and Auger electron spectroscopy are also able to study the depth-profile of semiconductor films. Table 1.11 demonstrates the comparison between those techniques with RBS.

Method	Destructive	Incident particle	Outgoing Particle	Detection limit	Depth resolution
RBS	No	Ion	Ion	~1	10 nm
XPS	Yes	X-ray photon	Electron	~0.1-1	~1 μm
EDX	Yes	Electron	X-ray photon	~0.1	1.5 nm
Auger	Yes	Electron	Electron	~0.1-1	1.5 nm

Table 1.11: Comparison between different thin film analysis techniques.

²⁴http://serc.carleton.edu/research_education/geochemsheets/eds.html

²⁵http://serc.carleton.edu/research_education/geochemsheets/wds.html

²⁶http://serc.carleton.edu/research_education/geochemsheets/BraggsLaw.html

²⁷<http://www.x-raymicroanalysis.com/x-ray-microanalysis-explained/pages/detectors/wave1.htm>

²⁸<http://micron.ucr.edu/public/manuals/EDS-intro.pdf>

²⁹This content is available online at <<http://cnx.org/content/m22411/1.3/>>.

1.11.2 Basic concept of Rutherford backscattering spectroscopy

At a basic level, RBS demonstrates the electrostatic repulsion between high energy incident ions and target nuclei. The specimen under study is bombarded with monoenergetic beam of $^4\text{He}^+$ particles and the backscattered particles are detected by the detector-analysis system which measures the energies of the particles. During the collision, energy is transferred from the incident particle to the target specimen atoms; the change in energy of the scattered particle depends on the masses of incoming and target atoms. For an incident particle of mass M_1 , the energy is E_0 while the mass of the target atom is M_2 . After the collision, the residual energy E of the particle scattered at angle $\emptyset$ can be expressed as:

$$E = k^2 E_0$$

$$k = \frac{\left(M_1 \cos \emptyset + \sqrt{M_2^2 - M_1^2 \sin^2 \emptyset} \right)}{M_1 + M_2}$$

where k is the kinematic scattering factor, which is actually the energy ratio of the particle before and after the collision. Since k depends on the masses of the incident particle and target atom and the scattering angle, the energy of the scattered particle is also determined by these three parameters. A simplified layout of backscattering experiment is shown in Figure 1 (Figure 1.88).

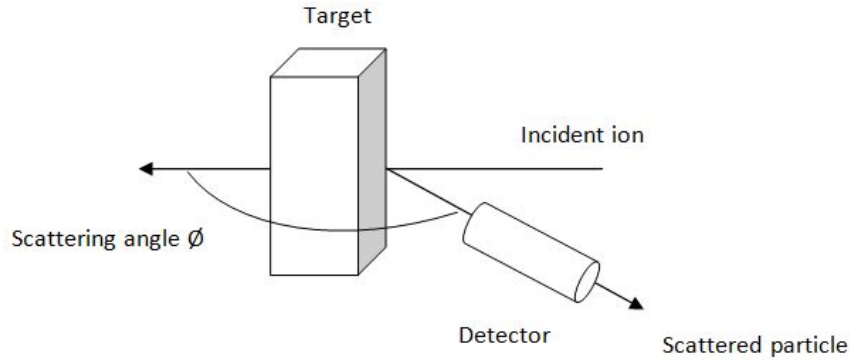


Figure 1.88: Schematic representation of the experimental setup for Rutherford backscattering analysis.

The probability of a scattering event can be described by the differential scattering cross section of a target atom for scattering an incoming particle through the angle $\emptyset$ into differential solid angle as follows,

$$\frac{d\sigma_R}{d\emptyset} = \left(\frac{zZe^2}{2E_0 \sin^2 \emptyset} \right) \frac{\left[\cos \emptyset + \sqrt{1 - \left(\frac{M_1}{M_2} \sin \emptyset \right)^2} \right]^2}{\sqrt{1 - \left(\frac{M_1}{M_2} \sin \emptyset \right)^2}}$$

where $d\sigma_R$ is the effective differential cross section for the scattering of a particle. The above equation

may look complicated but it conveys the message that the probability of scattering event can be expressed as a function of scattering cross section which is proportional to the zZ when a particle with charge ze approaches the target atom with charge Ze .

Helium ions not scattered at the surface lose energy as they traverse the solid. They lose energy due to interaction with electrons in the target. After collision the He particles lose further energy on their way out to the detector. We need to know two quantities to measure the energy loss, the distance Δt that the particles penetrate into the target and the energy loss ΔE in this distance Figure 1.89. The rate of energy loss or stopping power is a critical component in backscattering experiments as it determines the depth profile in a given experiment.

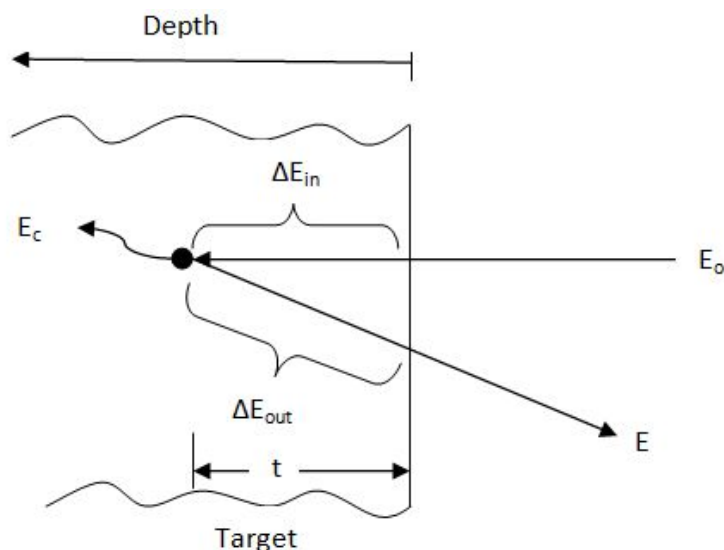


Figure 1.89: Components of energy loss for a ion beam that scatters from depth t . First, incident beam loses energy through interaction with electrons ΔE_{in} . Then energy lost occurs due to scattering E_c . Finally outgoing beam loses energy for interaction with electrons ΔE_{out} . Adapted from L. C. Feldman and J. W. Mayer, *Fundamentals of Surface and Thin Film Analysis*, North Holland-Elsevier, New York (1986).

In thin film analysis, it is convenient to assume that total energy loss ΔE into depth t is only proportional to t for a given target. This assumption allows a simple derivation of energy loss in backscattering as more complete analysis requires many numerical techniques. In constant dE/dx approximation, total energy loss becomes linearly related to depth t , Figure 1.90.

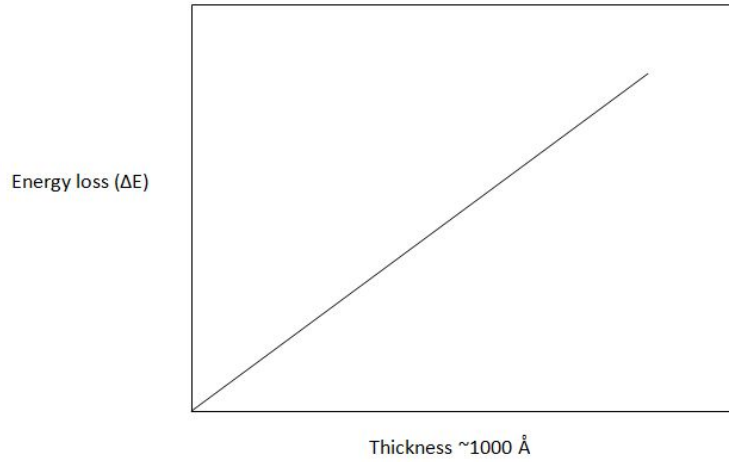


Figure 1.90: Variation of energy loss with the depth of the target in constant dE/dx approximation.

1.11.3 Experimental set-up

The apparatus for Rutherford backscattering analysis of thin solid surface typically consist of three components:

1. A source of helium ions.
2. An accelerator to energize the helium ions.
3. A detector to measure the energy of scattered ions.

There are two types of accelerator/ion source available. In single stage accelerator, the He^+ source is placed within an insulating gas-filled tank (Figure 1.91). It is difficult to install new ion source when it is exhausted in this type of accelerator. Moreover, it is also difficult to achieve particles with energy much more than 1 MeV since it is difficult to apply high voltages in this type of system.

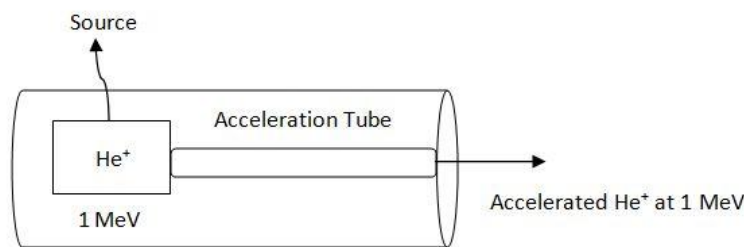


Figure 1.91: Schematic representation of a single stage accelerator.

Another variation is “tandem accelerator.” Here the ion source is at ground and produces negative ion. The positive terminal is located at the center of the acceleration tube (Figure 1.92). Initially the negative ion is accelerated from ground to terminal. At terminal two-electron stripping process converts the He^- to He^{++} . The positive ions are further accelerated toward ground due to columbic repulsion from positive terminal. This arrangement can achieve highly accelerated He^{++} ions (~ 2.25 MeV) with moderate voltage of 750 kV.

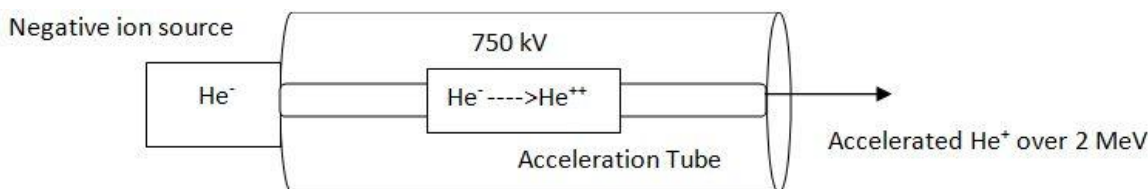


Figure 1.92: Schematic representation of a tandem accelerator.

Particles that are backscattered by surface atoms of the bombarded specimen are detected by a surface barrier detector. The surface barrier detector is a thin layer of p-type silicon on the n-type substrate resulting p-n junction. When the scattered ions exchange energy with the electrons on the surface of the detector upon reaching the detector, electrons get promoted from the valence band to the conduction band. Thus, each exchange of energy creates electron-hole pairs. The energy of scattered ions is detected by simply counting the number of electron-hole pairs. The energy resolution of the surface barrier detector in a standard RBS experiment is 12 - 20 keV. The surface barrier detector is generally set between 90° and 170° to the incident beam. Films are usually set normal to the incident beam. A simple layout is shown in Figure 1.93.

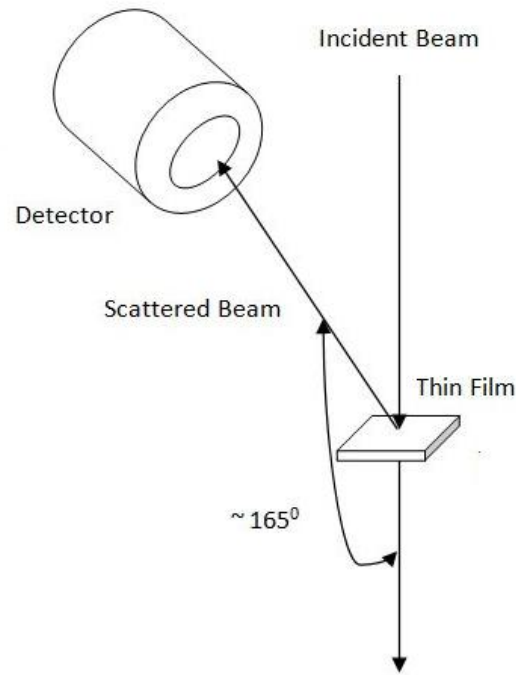


Figure 1.93: Schematic representation general setup where the surface barrier detector is placed at angle of 165° to the extrapolated incident beam.

1.11.4 Depth profile analysis

As stated earlier, it is a good approximation in thin film analysis that the total energy loss ΔE is proportional to depth t . With this approximation, we can derive the relation between energy width ΔE of the signal from a film of thickness Δt as follows,

$$\Delta E = \Delta t (k \frac{dE}{dx}_{in} + 1/\cos\theta \frac{dE}{dx}_{out})$$

where θ = lab scattering angle.

It is worth noting that k is the kinematic factor defined in equation above and the subscripts “in” and “out” indicate the energies at which the rate of loss of energy or dE/dx is evaluated. As an example, we consider the backscattering spectrum, at scattering angle 170° , for 2 MeV He^{++} incidents on silicon layer deposited onto 2 mm thick niobium substrate Figure 1.94.

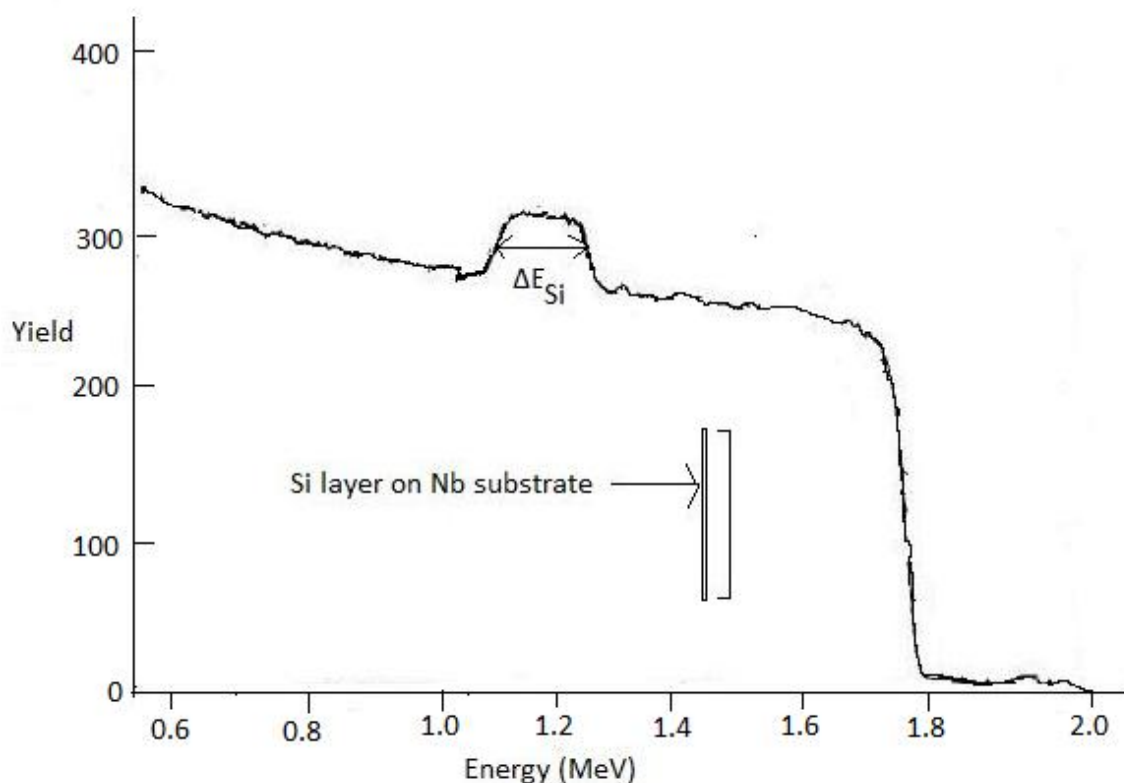


Figure 1.94: The backscattering spectrum for 2.0 MeV He ions incident on a silicon thin film deposited onto a niobium substrate. Adapted from P. D. Stupik, M. M. Donovan, A. R. Barron, T. R. Jervis and M. Nastasi, *Thin Solid Films*, 1992, **207**, 138.

The energy loss rate of incoming He^{++} or dE/dx along inward path in elemental Si is $\approx 24.6 \text{ eV/\AA}$ at 2 MeV and is $\approx 26 \text{ eV/\AA}$ for the outgoing particle at 1.12 MeV (Since K of Si is 0.56 when the scattering angle is 170° , energy of the outgoing particle would be equal to 2×0.56 or 1.12 MeV). Again the value of ΔE_{Si} is $\approx 133.3 \text{ keV}$. Putting the values into above equation we get

$$\begin{aligned} \Delta t &\approx 133.3 \text{ keV} / (0.56 * 24.6 \text{ eV/\AA} + 1/\cos 170^\circ * 26 \text{ eV/\AA}) \\ &= 133.3 \text{ keV} / (13.77 \text{ eV/\AA} + 29.985 \text{ eV/\AA}) \\ &= 133.3 \text{ keV} / 40.17 \text{ eV/\AA} \\ &= 3318 \text{ \AA}. \end{aligned}$$

Hence a Si layer of ca. 3300 $\text{\AA}$ thickness has been deposited on the niobium substrate. However we need to remember that the value of dE/dx is approximated in this calculation.

1.11.5 Quantitative Analysis

In addition to depth profile analysis, we can study the composition of an element quantitatively by backscattering spectroscopy. The basic equation for quantitative analysis is

$$Y = \sigma \cdot \Omega \cdot Q \cdot N \Delta t$$

Where Y is the yield of scattered ions from a thin layer of thickness Δt , Q is the number of incident ions and Ω is the detector solid angle, and $N\Delta t$ is the number of specimen atoms (atom/cm^2). shows the RBS spectrum for a sample of silicon deposited on a niobium substrate and subjected to laser mixing. The Nb has reacted with the silicon to form a NbSi_2 interphase layer. The Nb signal has broadened after the reaction as show in .

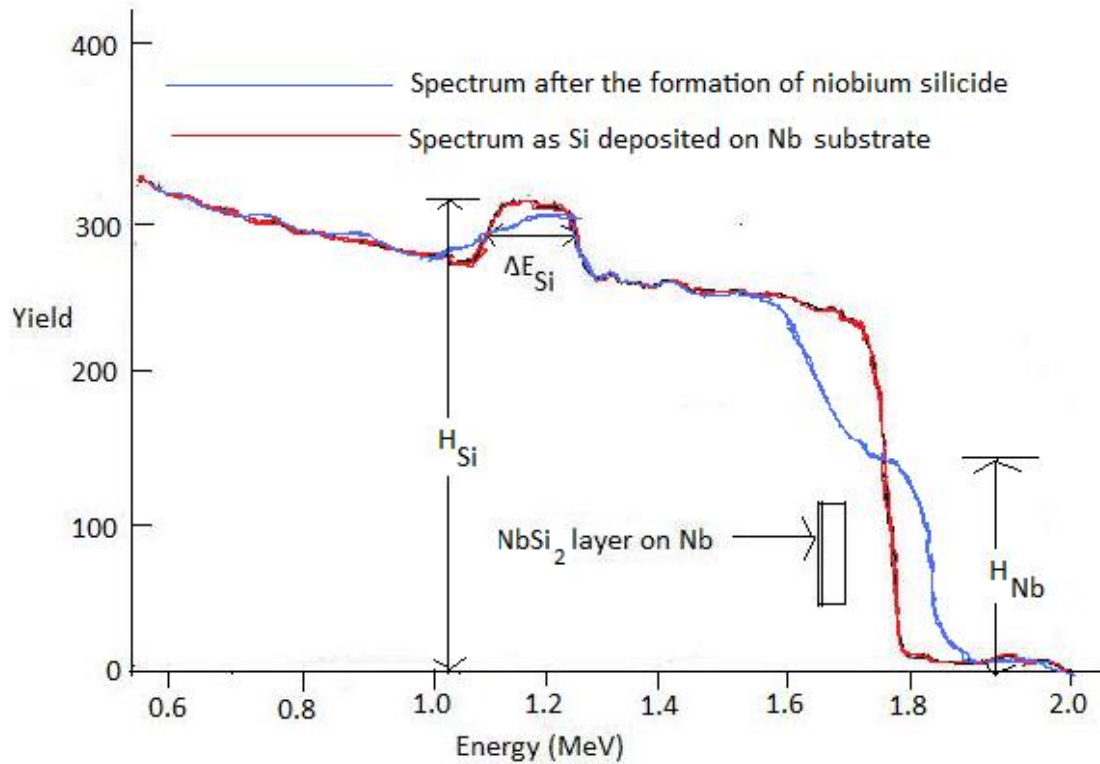


Figure 1.95: Backscattering spectra of Si diffused into Nb and Si as deposited on Nb substrate. Adapted from P. D. Stupik, M. M. Donovan, A. R. Barron, T. R. Jervis and M. Nastasi, *Thin Solid Films*, 1992, **207**, 138.

We can use ratio of the heights $H_{\text{Si}}/H_{\text{Nb}}$ of the backscattering spectrum after formation of NbSi_2 to determine the composition of the silicide layer. The stoichiometric ratio of Nb and Si can be approximated as,

$$N_{\text{Si}}/N_{\text{Nb}} \approx [H_{\text{Si}} * \sigma_{\text{Si}}]/[H_{\text{Nb}} * \sigma_{\text{Nb}}]$$

Hence the concentration of Si and Nb can be determined if we can know the appropriate cross sections σ_{Si} and σ_{Nb} . However the yield in the backscattering spectra is better represented as the product of signal height and the energy width ΔE . Thus stoichiometric ratio can be better approximated as

$$N_{\text{Si}}/N_{\text{Nb}} \approx [H_{\text{Si}} * \Delta E_{\text{Si}} * \sigma_{\text{Si}}]/[H_{\text{Nb}} * \Delta E_{\text{Nb}} * \sigma_{\text{Nb}}]$$

1.11.6 Limitations

It is of interest to understand the limitations of the backscattering technique in terms of the comparison with other thin film analysis technique such as AES, XPS and SIMS (Table 1.11). AES has better mass resolution, lateral resolution and depth resolution than RBS. But AES suffers from sputtering artifacts. Compared to RBS, SIMS has better sensitivity. RBS does not provide any chemical bonding information which we can get from XPS. Again, sputtering artifact problems are also associated in XPS. The strength of RBS lies in quantitative analysis. However, conventional RBS systems cannot analyze ultrathin films since the depth resolution is only about 10 nm using surface barrier detector.

1.11.7 Summary

Rutherford Backscattering analysis is a straightforward technique to determine the thickness and composition of thin films ($< 4000 \text{ \AA}$). Areas that have been lately explored are the use of backscattering technique in composition determination of new superconductor oxides; analysis of lattice mismatched epitaxial layers, and as a probe of thin film morphology and surface clustering.

1.11.8 Bibliography

- L. C. Feldman and J. W. Mayer, *Fundamentals of Surface and Thin Film Analysis*, North Holland-Elsevier, New York (1986).
- *Ion Spectroscopies for Surface Analysis*, Ed. A. W. Czanderna and D. M. Hercules, Plenum Press (New York), 1991.
- P. D. Stupik, M. M. Donovan, A. R. Barron, T. R. Jervis, and M. Nastasi, *Thin Solid Films*, 1992, **207**, 138

1.12 An Accuracy Assessment of the Refinement of Crystallographic Positional Metal Disorder in Molecular Solid Solutions ³⁰

1.12.1 Introduction

Crystallographic positional disorder is evident when a position in the lattice is occupied by two or more atoms; the average of which constitutes the bulk composition of the crystal. If a particular atom occupies a certain position in one unit cell and another atom occupies the same position in other unit cells, the resulting electron density will be a weight average of the situation in all the unit cells throughout the crystal. Since the diffraction experiment involves the average of a very large number of unit cells (ca. 10^{18} in a crystal used for single crystal X-ray diffraction analysis), minor static displacements of atoms closely simulate the effects of vibrations on the scattering power of the “average” atom. Unfortunately, the determination of the “average” atom in a crystal may be complicated if positional disorder is encountered.

Crystal disorder involving groups such as CO, CN and Cl have been documented to create problems in assigning the correct structure through refinement procedures. While attempts have been made to correlate crystallographic lattice parameters with bulk chemical composition of the solution from which single crystal was grown, there has been little effort to correlate crystallographic site occupancy with chemical composition of the crystal from which single crystal diffraction data was obtained. These are two very different issues that must be considered when solving a crystal structure with site occupancy disorder.

1. What is the relationship of a single crystal to the bulk material?
2. Is the refinement of a site-occupancy-factor actually gives a realistic value for % occupancy when compared to the "actual" % composition for that particular single crystal?

³⁰This content is available online at <http://cnx.org/content/m26148/1.2/>.

The following represents a description of a series of methods for the refinement of a site occupancy disorder between two atoms (e.g., two metal atoms within a mixture of isostructural compounds).

1.12.2 Methods for X-ray diffraction determination of positional disorder in molecular solid solutions

An atom in a structure is defined by several parameters: the type of atom, the positional coordinates (x, y, z), the occupancy factor (how many “atoms” are at that position) and atomic displacement parameters (often called temperature or thermal parameters). The latter can be thought of as being a “picture” of the volume occupied by the atom over all the unit cells, and can be isotropic (1 parameter defining a spherical volume) or anisotropic (6 parameters defining an ellipsoidal volume). For a “normal” atom, the occupancy factor is fixed as being equal to one, and the positions and displacement parameters are “refined” using least-squares methods to values in which the best agreement with the observed data is obtained. In crystals with site-disorder, one position is occupied by different atoms in different unit cells. This refinement requires a more complicated approach. Two broad methods may be used: either a new atom type that is the appropriate combination of the different atoms is defined, or the same positional parameters are used for different atoms in the model, each of which has occupancy values less than one, and for which the sum is constrained to total one. In both approaches, the relative occupancies of the two atoms are required. For the first approach, these occupancies have to be defined. For the second, the value can be refined. However, there is a relationship between the thermal parameter and the occupancy value so care must be taken when doing this. These issues can be addressed in several ways.

1.12.2.1 Method 1

The simplest assumption is that the crystal from which the X-ray structure is determined represents the bulk sample was crystallized. With this value, either a new atom type can be generated that is the appropriate combination of the measured atom type 1 (M) and atom type 2 (M') percent composition or two different atoms can be input with the occupancy factor set to reflect the percent composition of the bulk material. In either case the thermal parameters can be allowed to refine as usual.

1.12.2.2 Method 2

The occupancy values for two atoms (M and M') are refined (such that their sum was equal to 1), while the two atoms are constrained to have the same displacement parameters.

1.12.2.3 Method 3

The occupancy values (such that their sum was equal to 1) and the displacement parameters are refined independently for the two atoms.

1.12.2.4 Method 4

Once the best values for occupancy is obtained using either Methods 2 or 3, these values were fixed and the displacement parameters are allowed to refine freely.

1.12.3 A model system

Metal β -diketonate complexes (Figure 1.96) for metals in the same oxidation state are isostructural and often isomorphous. Thus, crystals obtained from co-crystallization of two or more metal β -diketonate complexes [e.g., $\text{Al}(\text{acac})_3$ and $\text{Cr}(\text{acac})_3$] may be thought of as a hybrid of the precursors; that is, the metal position in the crystal lattice may be defined as having the average metal composition.

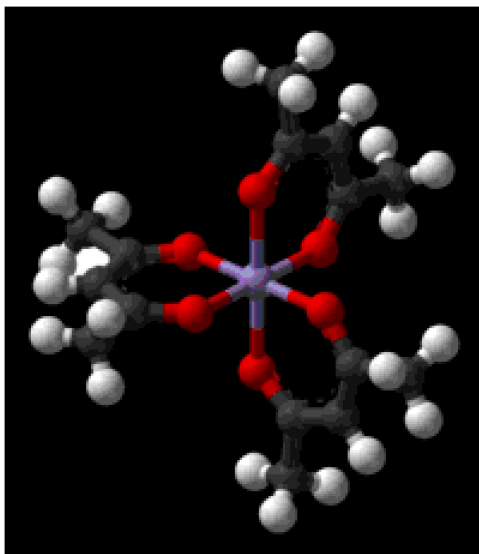


Figure 1.96: Molecular structure of $M(\text{acac})_3$, a typical metal β -diketonate complex.

A series of solid solutions of $\text{Al}(\text{acac})_3$ and $\text{Cr}(\text{acac})_3$ can be prepared for study by X-ray diffraction, by the crystallization from acetone solutions of specific mixtures of $\text{Al}(\text{acac})_3$ and $\text{Cr}(\text{acac})_3$ (Table 1.12, Column 1). The pure derivatives and the solid solution, $\text{Al}_{1-x}\text{Cr}_x(\text{acac})_3$, crystallize in the monoclinic space group $P2_1/c$ with $Z = 4$.

Solution composition (% Cr)	WDS composition of single crystal (% Cr)	Composition as refined from X-ray diffraction (% Cr)
13	1.9 ± 0.2	0 ^a
2	2.1 ± 0.3	0 ^a
20	17.8 ± 1.6	17.3 ± 1.8
26	26.7 ± 1.7	28.3 ± 1.9
18	48.5 ± 4.9	46.7 ± 2.1
60	75.1 ± 4.1	72.9 ± 2.4
80	91.3 ± 1.2	82.3 ± 3.1

Table 1.12: Variance in chromium concentrations (%) for samples of $\text{Al}_{1-x}\text{Cr}_x(\text{acac})_3$ crystallized from solutions of $\text{Al}(\text{acac})_3$ and $\text{Cr}(\text{acac})_3$. ^aConcentration too low to successfully refine the Cr occupancy.

Substitution of Cr for Al in the $M(\text{acac})_3$ structure could possibly occur in a random manner, i.e., a metal site has an equal probability of containing an aluminum or a chromium atom. Alternatively, if the chromium had preference for specific sites a super lattice structure of lower symmetry would be present. Such an ordering is not observed since all the samples show no additional reflections other than those that may be indexed to the monoclinic cell. Therefore, it may be concluded that the $\text{Al}(\text{acac})_3$ and $\text{Cr}(\text{acac})_3$ do indeed form solid solutions: $\text{Al}_{1-x}\text{Cr}_x(\text{acac})_3$.

Electron microprobe analysis, using wavelength-dispersive spectrometry (WDS), on the individual crystal from which X-ray crystallographic data was collected provides the “actual” composition of each crystal. Analysis was performed on at least 6 sites on each crystal using a 10 μm sized analysis spot providing a measure of the homogeneity within the individual crystal for which X-ray crystallographic data was collected. An example of a SEM image of one of the crystals and the point analyses is given in Figure 1.97. The data in Table 1.12 and Figure 1.97 demonstrate that while a batch of crystals may contain individual crystals with different compositions, each individual crystal is actually reasonably homogenous. There is, for most samples, a significant variance between the molar Al:Cr ratio in the bulk material and an individual crystal chosen for X-ray diffraction. The variation in Al:Cr ratio within each individual crystal ($\pm 10\%$) is much less than that between crystals.

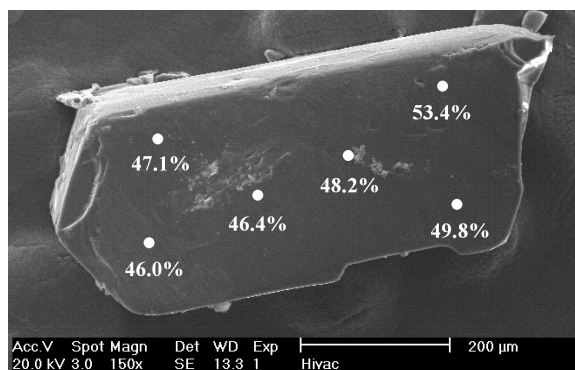


Figure 1.97: SEM image of a representative crystal used for WDS and X-ray diffraction analysis showing the location and results for the WDS analysis. The 10 μm sized analysis spots are represented by the white dots. Adapted from B. D. Fahlman, Ph.D. Thesis, Rice University, 2000.

1.12.4 Comparison of the methods

1.12.4.1 Method 1

Since Method 1 does not refine the %Cr and relies on an input for the Al and Cr percent composition of the "bulk" material, i.e., the %Cr in the total mass of the material (Table 1.12, Column 1), as opposed to the analysis of the single crystal on which X-ray diffraction was performed, (Table 1.12, Column 2), the closer these values were to the "actual" value determined by WDS for the crystal on which X-ray diffraction was performed (Table 1.12, Column 1 versus 2) then the closer the overall refinement of the structure to those of Methods 2 - 4.

While this assumption is obviously invalid for many of the samples, it is one often used when bulk data (for example, from NMR) is available. However, as there is no reason to assume that one crystal is completely representative of the bulk sample, it is unwise to rely only on such data.

1.12.4.2 Method 2

This method always produced final, refined, occupancy values that were close to those obtained from WDS (Table 1.12). This approach assumes that the motion of the central metal atoms is identical. While this is obviously not strictly true as they are of different size, the results obtained herein imply that this is a reasonable approximation where simple connectivity data is required. For samples where the amount of one

of the elements (i.e., Cr) is very low so low a good refinement can not often be obtained. In these cases, when refining the occupancy values, that for Al would exceed 1 while that of Cr would be less than 1!

1.12.4.3 Method 3

In some cases, despite the interrelationship between the occupancy and the displacement parameters, convergence was obtained successfully. In these cases the refined occupancies were both slightly closer to those observed from WDS than the occupancy values obtained using Method 2. However, for some samples with higher Cr content the refinement was unstable and would not converge. Whether this observation was due to the increased percentage of Cr or simply lower data quality is not certain.

While this method does allow refinement of any differences in atomic motion between the two metals, it requires extremely high quality data for this difference to be determined reliably.

1.12.4.4 Method 4

This approach adds little to the final results.

1.12.5 Correlation between analyzed composition and refined composition

Figure 1.98 shows the relationship between the chromium concentration (%Cr) determined from WDS and the refinement of X-ray diffraction data using Methods 2 or 3 (labeled in Figure 1.98). Clearly there exists a good correlation, with only a slight divergence at high Cr concentration. This is undoubtedly a consequence of trying to refine a low fraction of a light atom (Al) in the presence of a large fraction of a heavier atom (Cr). X-ray diffraction is, therefore, an accurate method of determining the M:M' ratios in crystalline solid solution.

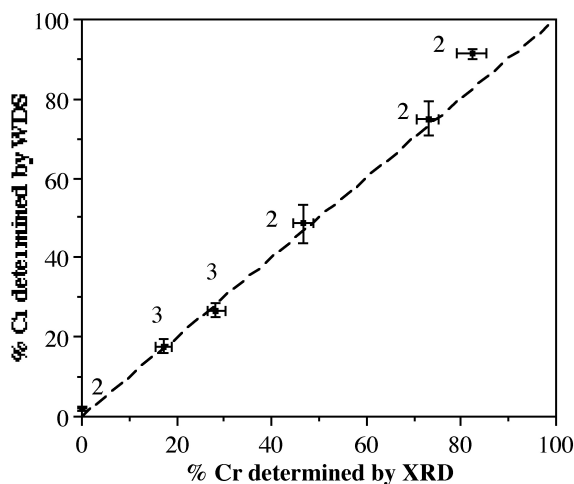


Figure 1.98: Comparison of the chromium concentration determined from WDS (with error) and refinement of X-ray diffraction data (with error) using Methods 2 or 3. Adapted from S. G. Bott, B. D. Fahlman, M. L. Pierson, and A. R. Barron, *J. Chem. Soc., Dalton Trans.*, 2001, 2148.

1.12.6 Bibliography

- S. G. Bott, B. D. Fahlman, M. L. Pierson, and A. R. Barron, *J. Chem. Soc., Dalton Trans.*, 2001, 2148.
- K. R. Dunbar and S. C. Haefner, *Inorg. Chem.*, 1992, **31**, 3676.
- J. Glusker, M. Lewis, and M., Rossi, *Crystal Structure Analysis for Chemists and Biologists* VCH: New York (1994).
- K. Yoon and G. Parkin, *Inorg. Chem.*, 1992, **114**, 31.

1.13 Principles of Gamma-ray Spectroscopy and Applications in Nuclear Forensics³¹

1.13.1 Introduction

Gamma-ray (γ -ray) spectroscopy is a quick and nondestructive analytical technique that can be used to identify various radioactive isotopes in a sample. In gamma-ray spectroscopy, the energy of incident gamma-rays is measured by a detector. By comparing the measured energy to the known energy of gamma-rays produced by radioisotopes, the identity of the emitter can be determined. This technique has many applications, particularly in situations where rapid nondestructive analysis is required.

1.13.2 Background principles

1.13.2.1 Radioactive decay

The field of chemistry typically concerns itself with the behavior and interactions of stable isotopes of the elements. However, elements can exist in numerous states which are not stable. For example, a nucleus can have too many neutrons for the number of protons it has or contrarily, it can have too few neutrons for the number of protons it has. Alternatively, the nuclei can exist in an excited state, wherein a nucleon is present in an energy state that is higher than the ground state. In all of these cases, the unstable state is at a higher energy state and the nucleus must undergo some kind of decay process to reduce that energy.

There are many types of radioactive decay, but type most relevant to gamma-ray spectroscopy is gamma decay. When a nucleus undergoes radioactive decay by α or β decay, the resultant nucleus produced by this process, often called the daughter nucleus, is frequently in an excited state. Similar to how electrons are found in discrete energy levels around a nucleus, nucleons are found in discrete energy levels within the nucleus. In γ decay, the excited nucleon decays to a lower energy state and the energy difference is emitted as a quantized photon. Because nuclear energy levels are discrete, the transitions between energy levels are fixed for a given transition. The photon emitted from a nuclear transition is known as a γ -ray.

1.13.2.2 Radioactive decay kinetics and equilibria

Radioactive decay, with few exceptions, is independent of the physical conditions surrounding the radioisotope. As a result, the probability of decay at any given instant is constant for any given nucleus of that particular radioisotope. We can use calculus to see how the number of parent nuclei present varies with time. The time constant, λ , is a representation of the rate of decay for a given nuclei, (1.59).

$$\frac{dN}{N} = -\lambda dt \quad (1.59)$$

If the symbol N_0 is used to represent the number of radioactive nuclei present at $t = 0$, then the following equation describes the number of nuclei present at some given time.

$$N = N_0 e^{-\lambda t} \quad (1.60)$$

³¹This content is available online at <<http://cnx.org/content/m38345/1.1/>>.

The same equation can be applied to the measurement of radiation with some sort of detector. The count rate will decrease from some initial count rate in the same manner that the number of nuclei will decrease from some initial number of nuclei.

The decay rate can also be represented in a way that is more easily understood. The equation describing half-life ($t_{1/2}$) is shown in (1.61).

$$t_{1/2} = \frac{\ln 2}{\lambda} \quad (1.61)$$

The half-life has units of time and is a measure of how long it takes for the number of radioactive nuclei in a given sample to decrease to half of the initial quantity. It provides a conceptually easy way to compare the decay rates of two radioisotopes. If one has the same number of starting nuclei for two radioisotopes, one with a short half-life and one with a long half-life, then the count rate will be higher for the radioisotope with the short half-life, as many more decay events must happen per unit time in order for the half-life to be shorter.

When a radioisotope decays, the daughter product can also be radioactive. Depending upon the relative half-lives of the parent and daughter, several situations can arise: no equilibrium, a transient equilibrium, or a secular equilibrium. This module will not discuss the former two possibilities, as they are of less relevance to this particular discussion.

Secular equilibrium takes place when the half-life of the parent is much longer than the half-life of the daughter. In any arbitrary equilibrium, the ratio of atoms of each can be described as in (1.62).

$$\frac{N_p}{N_d} = \frac{\lambda_d - \lambda_p}{\lambda_p} \quad (1.62)$$

Because the half-life of the parent is much, much greater than the daughter, as the parent decays, the observed amount of activity changes very little.

$$\frac{N_p}{N_d} = \frac{\lambda_d}{\lambda_p} \quad (1.63)$$

This can be rearranged to show that the activity of the daughter should equal the activity of the parent.

$$A_p = A_d \quad (1.64)$$

Once this point is reached, the parent and the daughter are now in secular equilibrium with one another and the ratio of their activities should be fixed. One particularly useful application of this concept, to be discussed in more detail later, is in the analysis of the refinement level of long-lived radioisotopes that are relevant to trafficking.

1.13.3 Detectors

1.13.3.1 Scintillation detector

A scintillation detector is one of several possible methods for detecting ionizing radiation. Scintillation is the process by which some material, be it a solid, liquid, or gas, emits light in response to incident ionizing radiation. In practice, this is used in the form of a single crystal of sodium iodide that is doped with a small amount of thallium, referred to as NaI(Tl). This crystal is coupled to a photomultiplier tube which converts the small flash of light into an electrical signal through the photoelectric effect. This electrical signal can then be detected by a computer.

1.13.3.2 Semiconductor detector

A semiconductor accomplishes the same effect as a scintillation detector, conversion of gamma radiation into electrical pulses, except through a different route. In a semiconductor, there is a small energy gap between

the valence band of electrons and the conduction band. When a semiconductor is hit with gamma-rays, the energy imparted by the gamma-ray is enough to promote electrons to the conduction band. This change in conductivity can be detected and a signal can be generated correspondingly. Germanium crystals doped with lithium, Ge(Li), and high-purity germanium (HPGe) detectors are among the most common types.

1.13.3.3 Advantages and disadvantages

Each detector type has its own advantages and disadvantages. The NaI(Tl) detectors are generally inferior to Ge(Li) or HPGe detectors in many respects, but are superior to Ge(Li) or HPGe detectors in cost, ease of use, and durability. Germanium-based detectors generally have much higher resolution than NaI(Tl) detectors. Many small photopeaks are completely undetectable on NaI(Tl) detectors that are plainly visible on germanium detectors. However, Ge(Li) detectors must be kept at cryogenic temperatures for the entirety of their lifetime or else they rapidly become incapable of functioning as a gamma-ray detector. Sodium iodide detectors are much more portable and can even potentially be used in the field because they do not require cryogenic temperatures so long as the photopeak that is being investigated can be resolved from the surrounding peaks.

1.13.3.4 Gamma spectrum features

There are several dominant features that can be observed in a gamma spectrum. The dominant feature that will be seen is the photopeak. The photopeak is the peak that is generated when a gamma-ray is totally absorbed by the detector. Higher density detectors and larger detector sizes increase the probability of the gamma-ray being absorbed.

The second major feature that will be observed is that of the Compton edge and distribution. The Compton edge arises due to Compton Effect, wherein a portion of the energy of the gamma-ray is transferred to the semiconductor detector or the scintillator. This occurs when the relatively high energy gamma ray strikes a relatively low energy electron. There is a relatively sharp edge to the Compton edge that corresponds to the maximum amount of energy that can be transferred to the electron via this type of scattering. The broad peak lower in energy than the Compton edge is the Compton distribution and corresponds to the energies that result from a variety of scattering angles. A feature in Compton distribution is the backscatter peak. This peak is a result of the same effect but corresponds to the minimum energy amount of energy transferred. The sum of the energies of the Compton edge and the backscatter peak should yield the energy of the photopeak.

Another group of features in a gamma spectrum are the peaks that are associated with pair production. Pair production is the process by which a gamma ray of sufficiently high energy (>1.022 MeV) can produce an electron-positron pair. The electron and positron can annihilate and produce two 0.511 MeV gamma photons. If all three gamma rays, the original with its energy reduced by 1.022 MeV and the two annihilation gamma rays, are detected simultaneously, then a full energy peak is observed. If one of the annihilation gamma rays is not absorbed by the detector, then a peak that is equal to the full energy less 0.511 MeV is observed. This is known as an escape peak. If both annihilation gamma rays escape, then a full energy peak less 1.022 MeV is observed. This is known as a double escape peak.

1.13.4 Example of experiments

1.13.4.1 Determination of depleted uranium

Natural uranium is composed mostly of ^{238}U with low levels of ^{235}U and ^{234}U . In the process of making enriched uranium, uranium with a higher level of ^{235}U , depleted uranium is produced. Depleted uranium is used in many applications particularly for its high density. Unfortunately, uranium is toxic and is a potential health hazard and is sometimes found in trafficked radioactive materials, so it is important to have a methodology for detection and analysis of it.

One easy method for this determination is achieved by examining the spectrum of the sample and comparing it qualitatively to the spectrum of a sample that is known to be natural uranium. This type of

qualitative approach is not suitable for issues that are of concern to national security. Fortunately, the same approach can be used in a quantitative fashion by examining the ratios of various gamma-ray photopeaks.

The concept of a radioactive decay chain is important in this determination. In the case of ^{238}U , it decays over many steps to ^{206}Pb . In the process, it goes through $^{234\text{m}}\text{Pa}$, ^{234}Pa , and ^{234}Th . These three isotopes have detectable gamma emissions that are capable of being used quantitatively. As can be seen in Table 1.13, the half-life of these three emitters is much less than the half-life of ^{238}U . As a result, these should exist in secular equilibrium with ^{238}U . Given this, the ratio of activity of ^{238}U to each daughter products should be 1:1. They can thus be used as a surrogate for measuring ^{238}U decay directly via gamma spectroscopy. The total activity of the ^{238}U can be determined by (1.65), where A is the total activity of ^{238}U , R is the count rate of the given daughter isotope, and B is the probability of decay via that mode. The count rate may need to be corrected for self-absorption of the sample is particularly thick. It may also need to be corrected for detector efficiency if the instrument does not have some sort of internal calibration.

$$A = R/B \quad (1.65)$$

Isotope	Half-life
^{238}U	4.5×10^9 years
^{234}Th	24.1 days
$^{234\text{m}}\text{Pa}$	1.17 minutes

Table 1.13: Half-lives of pertinent radioisotopes in the ^{238}U decay chain

Exercise 1.13.1

(Solution on p. 117.)

A gamma spectrum of a sample is obtained. The 63.29 keV photopeak associated with ^{234}Th was found to have a count rate of 5.980 kBq. What is the total activity of ^{238}U present in the sample?

The count rate of ^{235}U can be observed directly with gamma spectroscopy. This can be converted, as was done in the case of ^{238}U above, to the total activity of ^{235}U present in the sample. Given that the natural abundances of ^{238}U and ^{235}U are known, the ratio of the expected activity of ^{238}U to ^{235}U can be calculated to be 21.72 : 1. If the calculated ratio of disintegration rates varies significantly from this expected value, then the sample can be determined to be depleted or enriched.

Exercise 1.13.2

(Solution on p. 117.)

As shown above, the activity of ^{238}U in a sample was calculated to be 123.6 kBq. If the gamma spectrum of this sample shows a count rate 23.73 kBq at the 185.72 keV photopeak for ^{235}U , can this sample be considered enriched uranium? The emission probability for this photopeak is 57.2%.

This type of calculation is not unique to ^{238}U . It can be used in any circumstance where the ratio of two isotopes needs to be compared so long as the isotope itself or a daughter product it is in secular equilibrium with has a usable gamma-ray photopeak.

1.13.4.2 Determination of the age of highly-enriched uranium

Particularly in the investigation of trafficked radioactive materials, particularly fissile materials, it is of interest to determine how long it has been since the sample was enriched. This can help provide an idea of the source of the fissile material—if it was enriched for the purpose of trade or if it was from cold war era enrichment, etc.

When uranium is enriched, ^{235}U is concentrated in the enriched sample by removing it from natural uranium. This process will separate the uranium from its daughter products that it was in secular equilibrium with. In addition, when ^{235}U is concentrated in the sample, ^{234}U is also concentrated due to the particulars of the enrichment process. The ^{234}U that ends up in the enriched sample will decay through

several intermediates to ^{214}Bi . By comparing the activities of ^{234}U and ^{214}Bi or ^{226}Ra , the age of the sample can be determined.

$$A_{\text{Bi}} = A_{\text{Ra}} = \frac{A_{\text{U}}}{2} \lambda_{\text{Th}} \lambda_{\text{Ra}} T^2 \quad (1.66)$$

In (1.66), A_{Bi} is the activity of ^{214}Bi , A_{Ra} is the activity of ^{226}Ra , A_{U} is the activity of ^{234}U , λ_{Th} is the decay constant for ^{230}Th , λ_{Ra} is the decay constant for ^{226}Ra , and T is the age of the sample. This is a simplified form of a more complicated equation that holds true over all practical sample ages (on the order of years) due to the very long half-lives of the isotopes in question. The results of this can be graphically plotted as they are in .

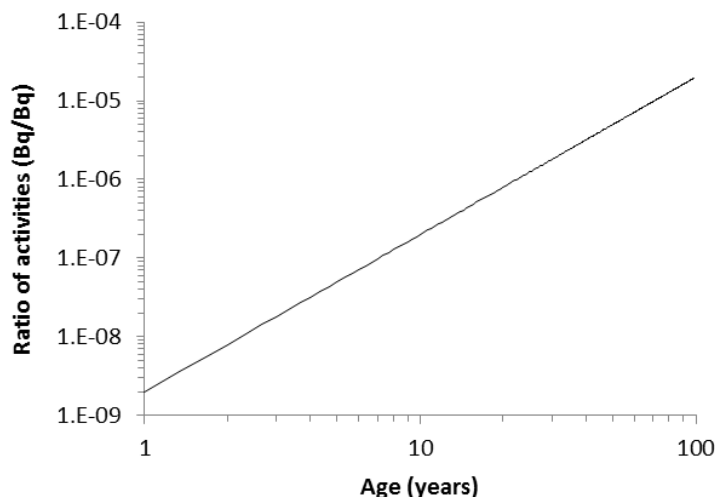


Figure 1.99: Ratio of $^{226}\text{Ra}/^{234}\text{U}$ ($= ^{214}\text{Bi}/^{234}\text{U}$) plotted versus age based on (1.66). This can be used to determine how long ago a sample was enriched based on the activities of ^{234}U and ^{226}Ra or ^{214}Bi in the sample.

Exercise 1.13.3

(Solution on p. 118.)

Exercise: The gamma spectrum for a sample is obtained. The count rate of the 121 keV ^{234}U photopeak is 4500 counts per second and the associated emission probability is 0.0342%. The count rate of the 609.3 keV ^{214}Bi photopeak is 5.83 counts per second and the emission probability is 46.1%. How old is the sample?

1.13.5 References

- G. Choppin, J.-O. Liljenzin, and J. Rydberg. *Radiochemistry and Nuclear Chemistry*, Elsevier Press, Oxford (2006).
- W. Loveland, D. J. Morrissey, and G. T. Seaborg. *Modern Nuclear Chemistry*, Wiley, New Jersey (2006).
- K. Mayer, M. Wallenius, and I. Ray. *Analyst*, 2005, **130**, 433.

- J. T. Mihalczo, J. A. Mullens, J. K. Mattingly, and T. E. Valentine. *Nucl. Instrum. Meth. A*, 2000, **450**, 531.
- J. T. Mihalczo, J. K. Mattingly, J. S. Neal, and J. A. Mullens, *Nucl. Instrum. Meth. B*, 2004, **213**, 378.
- K. J. Moody, I. A. Hutcheon, and P. M. Grant. *Nuclear Forensic Analysis*, CRC Press, Boca Raton (2005).
- C. T. Nguyen. *Nucl. Instrum. Meth. B*, 2005, **229**, 103.
- C. T. Nguyen, and J. Zsigrai. *Nucl. Instrum. Meth. B*, 2006, **246**, 417.
- D. Reilly, N. Ensslin, and H. Smith, Jr. *Passive Nondestructive Assay of Nuclear Materials*, National Technical Information Service, Springfield, VA (1991).
- M. Wallenius, A. Morgenstern, C. Apostolidis, and K. Mayer. *Anal. Bioanal. Chem.*, 2002, **374**, 379.

Solutions to Exercises in Chapter 1

Solution to Exercise 1.4.1 (p. 37)

The fuel mole fraction is 4.03%.

Solution to Exercise 1.4.2 (p. 40)

The empirical formula is C_3H_7 , and the molecular formula is $(C_3H_7)_6$ or $C_{18}H_{42}$.

Solution to Exercise 1.4.3 (p. 42)

The empirical formula is C_4H_8O , and the molecular formula is $(C_4H_8O)_2$ or $C_8H_{16}O_2$. Possible compounds with this molecular formula are shown in (Figure 1.100).

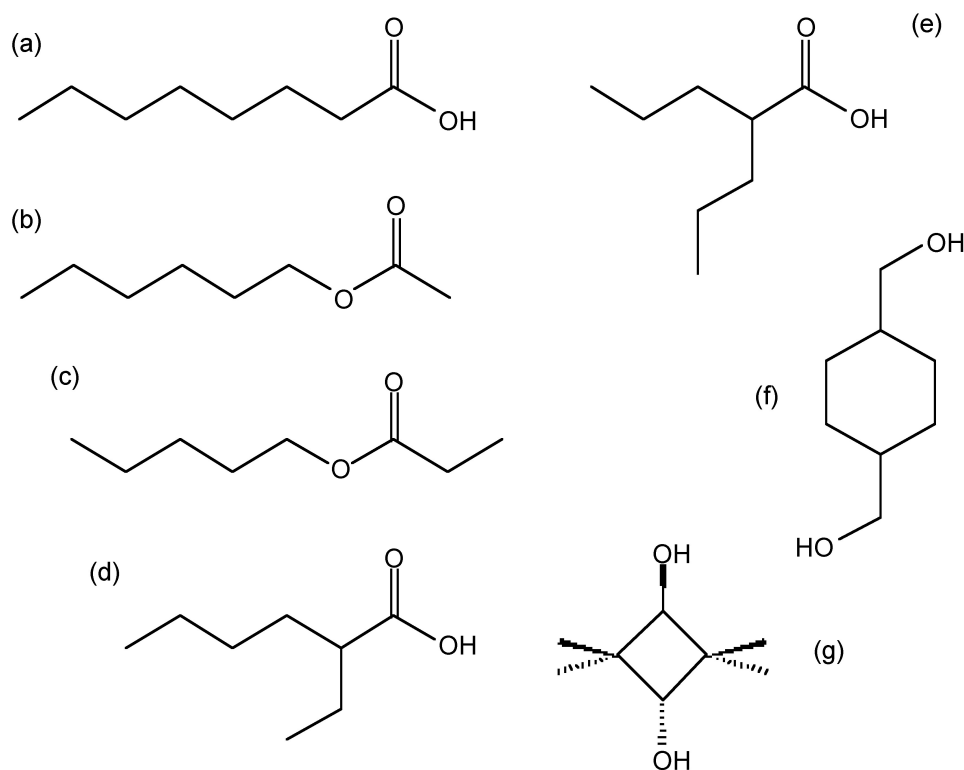


Figure 1.100: Structure of possible compounds with the molecular formula $C_8H_{16}O_2$: (a) octanoic acid (caprylic acid), (b) hexyl acetate, (c) pentyl propanoate, (d) 2-ethyl hexanoic acid, (e) valproic acid (VPA), (f) cyclohexanedimethanol (CHDM), and (g) 2,2,4,4-tetramethyl-1,3-cyclobutandiol (CBDO).

Solution to Exercise 1.4.4 (p. 43)

The chemical formula is Cu_2O , and Cu has a 1+ oxidation state.

Solution to Exercise 1.13.1 (p. 114)

^{234}Th exists in secular equilibrium with ^{238}U . The total activity of ^{234}Th must be equal to the activity of the ^{238}U . First, the observed activity must be converted to the total activity using Equation $A=R/B$. It is known that the emission probability for the 63.29 keV gamma-ray for ^{234}Th is 4.84%. Therefore, the total activity of ^{238}U in the sample is 123.6 kBq.

Solution to Exercise 1.13.2 (p. 114)

As shown in the example above, the count rate can be converted to a total activity for ^{235}U . This yields a total activity of 41.49 kBq for ^{235}U . The ratio of activities of ^{238}U and ^{235}U can be calculated to be 2.979.

This is lower than the expected ratio of 21.72, indicating that the ^{235}U content of the sample greater than the natural abundance of ^{235}U .

Solution to Exercise 1.13.3 (p. 115)

Solution: The observed count rates can be converted to the total activities for each radionuclide. Doing so yields a total activity for ^{234}U of 4386 kBq and a total activity for ^{214}Bi of 12.65 Bq. This gives a ratio of 9.614×10^{-7} . Using , as graphed this indicates that the sample must have been enriched 22.0 years prior to analysis.

Chapter 2

Physical and Thermal Analysis

2.1 Melting Point Analysis ¹

2.1.1 Introduction

Melting point (Mp) is a quick and easy analysis that may be used to qualitatively identify relatively pure samples (approximately <10% impurities). It is also possible to use this analysis to quantitatively determine purity. Melting point analysis, as the name suggests, characterizes the melting point, a stable physical property, of a sample in a straightforward manner, which can then be used to identify the sample.

2.1.2 Equipment

Although different designs of apparatus exist, they all have some sort of heating or heat transfer medium with a control, a thermometer, and often a backlight and magnifying lens to assist in observing melting (Figure 2.1). Most models today utilize capillary tubes containing the sample submerged in a heated oil bath. The sample is viewed with a simple magnifying lens. Some new models have digital thermometers and controls and even allow for programming. Programming allows more precise control over the starting temperature, ending temperature and the rate of change of the temperature.

¹This content is available online at <<http://cnx.org/content/m43565/1.1/>>.

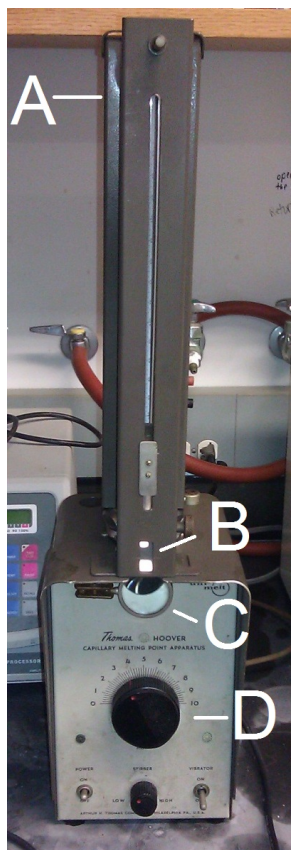


Figure 2.1: A Thomas Hoover melting point apparatus. The tower (A) contains a thermometer with a reflective view (B), so that the sample and temperature may be monitored simultaneously. The magnifying lens (C) allows better viewing of samples and lies above the heat controller (D).

2.1.3 Sample preparation

For melting point analysis, preparation is straight forward. The sample must be thoroughly dried and relatively pure ($<10\%$ impurities). The dry sample should then be packed into a melting point analysis capillary tube, which is simply a glass capillary tube with only one open end. Only 1 to 3 mm of sample is needed for sufficient analysis. The sample needs to be packed down into the closed end of the tube. This may be done by gently tapping the tube or dropping it upright onto a hard surface (Figure 2.2). Some apparatuses have a vibrator to assist in packing the sample. Finally the tube should be placed into the machine. Some models can accommodate multiple samples.

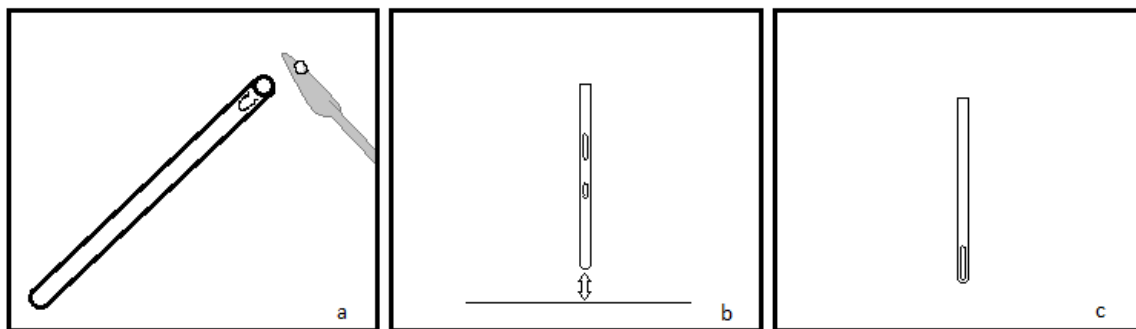


Figure 2.2: Schematic showing how to pack dried sample into a melting point analysis capillary tube: (a) using a spatula, push a sufficient amount of sample into the tube opening, (b) using a tapping motion or dropping the tube, pack the sample into the closed end, (c) the sample is ready to be loaded into the apparatus.

2.1.4 Recording data

Performing analysis is different from machine to machine, but the overall process is the same (Figure 2.3). If possible, choose a starting temperature, ending temperature, and rate of change of temperature. If the identity of the sample is known, base the starting and ending temperatures from the known melting point of the chemical, providing margins on both sides of the range. If using a model without programming, simply turn on the machine and monitor the rate of temperature change manually.

This media object is a Flash object. Please view or download it at
<http://www.youtube.com/v/9RNRYLvIbXM?version=3&hl=en_US>

Figure 2.3: A video discussing sample preparation, recording data and melting point analysis in general. Made by Indiana University-Purdue University Indianapolis chemistry department.

Visually inspect the sample as it heats. Once melting begins, note the temperature. When the sample is completely melted, note the temperature again. That is the melting point range for the sample. Pure samples typically have a 1 - 2 °C melting point range, however, this may be broadened due to colligative properties.

2.1.5 Interpreting data

There are two primary uses of melting point analysis data. The first is for qualitative identification of the sample, and the second is for quantitative purity characterization of the sample.

For identification, compare the experimental melting point range of the unknown to literature values. There are several vast databases of these values. Obtain a pure sample of the suspected chemical and mix a small amount of the unknown with it and conduct melting point analysis again. If a sharp melting point

range is observed at similar temperatures to the literature values, then the unknown has likely been identified correctly. Conversely, if the melting point range is depressed or broadened, which would be due to colligative properties, then the unknown was not successfully identified.

To characterize purity, first the identity of the solvent (the main constituent of the sample) and the identity of the primary solute need to be known. This may be done using other forms of analysis, such as gas chromatography-mass spectroscopy coupled with a database. Because melting point depression is unique between chemicals, a mixed melting curve comparing molar fractions of the two constituents with melting point needs to either be obtained or prepared (Figure 2.4). Simply prepare standards with known molar fraction ratios, then perform melting point analysis on each standard and plot the results. Compare the melting point range of the experimental sample to the curve to identify the approximate molar fractions of the constituents. This sort of purity characterization cannot be performed if there are more than two primary components to the sample.

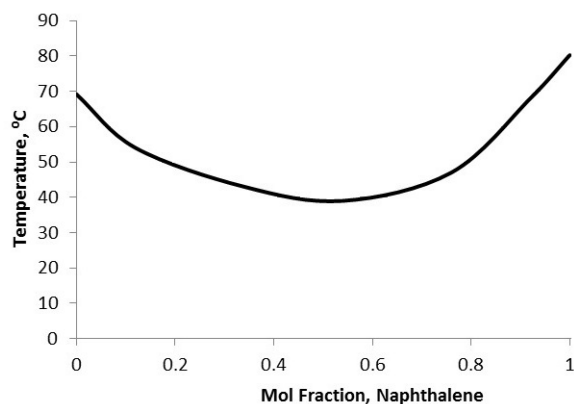


Figure 2.4: A mixed melting curve for naphthalene and biphenyl. Non-pure samples exhibit melting point depression due to colligative properties. Adapted from “Melting Point Analysis”, Chem 211L, Clark College protocol.

2.1.6 Specificity and accuracy

Melting point analysis is fairly specific and accurate given its simplicity. Because melting point is a unique physical characteristic of a substance, melting point analysis does have high specificity. Although, many substances have similar melting points, so having an idea of possible chemicals in mind can greatly narrow down the choices. The thermometers used are also accurate. However, melting point is dependent on pressure as well, so experimental results can vary from literature values, especially at extreme locations, i.e., places of high altitude. The biggest source of error stems from the visual detection of melting by the experimenter. Controlling the change rate and running multiple trials can lessen the degree of error introduced at this step.

2.1.7 Advantages of melting point analysis

Melting point analysis is a quick, relatively easy, and inexpensive preliminary analysis if the sample is already mostly pure and has a suspected identity. Additionally, analysis requires small samples only.

2.1.8 Limitations of melting point analysis

As with any analysis, there are certain drawbacks to melting point analysis. If the sample is not solid, melting point analysis cannot be done. Also, analysis is destructive of the sample. For qualitative identification analysis, there are now more specific and accurate analyses that exist, although they are typically much more expensive. Also, samples with more than one solute cannot be analyzed quantitatively for purity.

2.1.9 Bibliography

- IUPUIORGANICCHEM, “Exp 3 Melting Point Determination”, <http://www.youtube.com/watch?v=9RNRyLvlbXM>², April 2012.
- C. E. Bell, D. Taber, and K. Clark, *Organic Chemistry Laboratory: Standard and Microscale Experiments*, 2nd Edition, Saunders College Publishing, San Diego (1997).
- J. W. Zubrick, *The Organic Chem Lab Survival Guide*, John Wiley & Sons, Inc., Chichester (1988).
- “Melting Point Analysis” protocol. Chem 211, Clark College (2007).
- D. A. Straus, *Melting Point Analysis*, <http://www.chemistry.sjsu.edu/straus/MP%20htms/MP1measure.htm>³, April, 2012.
- *Thomas Hoover Melting Point Apparatus*, <http://www.jce.divched.org/JCEsoft/CCA/CCA6/MAIN/1ChemLabMenu/1>, April, 2012.

2.2 Solution Molecular Weight of Small Molecules⁵

2.2.1 Introduction

The cryoscopic method was formally introduced in the 1880’s when François-Marie Raoult (Figure 2.5) published how solutes depressed the freezing points of various solvents such as benzene, water, and formic acid. He concluded from his experimentation “if one molecule of a substance can be dissolved in one-hundred molecules of any given solvent then the solvent temperature is lowered by a specific temperature increment”. Based on Raoult’s research, Ernst Otto Beckmann (Figure 2.6) invented the Beckmann thermometer and the associated freezing - point apparatus (Figure 2.7), which was a significant improvement in measuring freezing - point depression values for a pure solvent. The simplicity, ease, and accuracy of this apparatus has allowed it to remain as a current standard with few modifications for molecular weight determination of unknown compounds.

²<http://www.youtube.com/watch?v=9RNRyLvlbXM>

³<http://www.chemistry.sjsu.edu/straus/MP%20htms/MP1measure.htm>

⁴http://www.jce.divched.org/JCEsoft/CCA/CCA6/MAIN/1ChemLabMenu/Measuring/Temperature/meltpoint_menu/meltpoint_menu_4/MENU

⁵This content is available online at <<http://cnx.org/content/m43553/1.1/>>.



Figure 2.5: French chemist François-Marie Raoult (1830 - 1901).



Figure 2.6: German chemist Ernst Otto Beckmann (1853 - 1923).

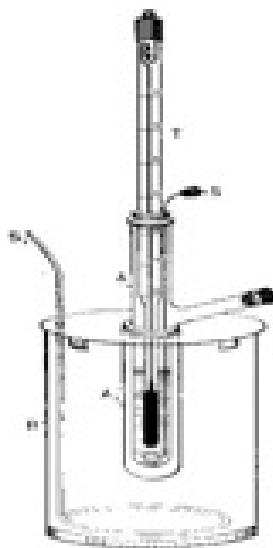


Figure 2.7: Beckmann differential thermometer and freezing point depression apparatus

The historical significance of Raoult and Beckmann's research, among many other investigators, has revolutionized a physical chemistry technique that is currently applied to a vast range of disciplines from food science to petroleum fluids. For example, measured cryoscopic molecular weights of crude oil are used to predict the viscosity and surface tension for necessary fluid flow calculations in pipeline.

2.2.2 Freezing point depression

Freezing point depression is a colligative property in which the freezing temperature of a pure solvent decreases in proportion to the number of solute molecules dissolved in the solvent. The known mass of the added solute and the freezing point of the pure solvent information permit an accurate calculation of the molecular weight of the solute.

In (2.1) the freezing point depression of a non-ionic solution is described. Where ΔT_f is the change in the initial and final temperature of the pure solvent, K_f is the freezing point depression constant for the pure solvent, and m (moles solute/kg solvent) is the molality of the solution.

$$\Delta T_f = K_f m \quad (2.1)$$

For an ionic solution shown in (2.2), the dissociation particles must be accounted for with the number of solute particles per formula unit, i (the van't Hoff factor).

$$\Delta T_f = K_f m i \quad (2.2)$$

2.2.3 Cryoscopic procedure

2.2.3.1 Cryoscopic apparatus

For cryoscopy, the apparatus to measure freezing point depression of a pure solvent may be representative of the Beckmann apparatus previously shown in Figure 2.7. The apparatus consists of a test tube containing

the solute dissolved in a pure solvent, stir bar or magnetic wire and closed with a rubber stopper encasing a mercury thermometer. The test tube component is immersed in an ice-water bath in a beaker. An example of the apparatus is shown in . The rubber stopper and stir bar/wire stirrer are not shown in the figure.

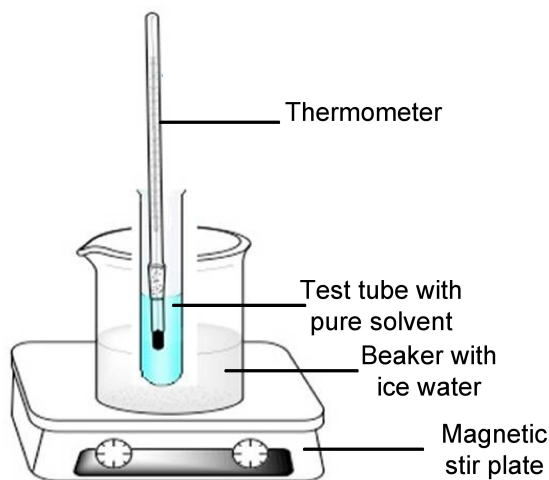


Figure 2.8: An example of a cryoscopic apparatus. Adapted from <http://www.lahc.cc.ca.us/classes/chemistry/arias/Exp%2012%20-%20Freezing%20Point.pdf>

2.2.3.2 Sample and solvent selection

The cryoscopic method may be used for a wide range of samples with various degrees of polarity. The solute and solvent selection should follow the premise of like dissolved like or in terms of Raoult's principle of the dissolution of one molecule of solute in one-hundred molecules of a solvent. The most common solvents such as benzene are generally selected because it is unreactive, volatile, and miscible with many compounds. Table 2.1 shows the cryoscopic constants (K_f) for the common solvents used for cryoscopy. A complete list of K_f values are available in Knovel Critical Tables.

Compound	K_f
Acetic Acid	3.90
Benzene	5.12
Camphor	39.7
Carbon disulfide	3.8
Carbon tetrachloride	30
Chloroform	4.68
Cyclohexane	20.2
Ethanol	1.99
Naphthalene	6.80
Phenol	7.27
Water	1.86

Table 2.1: Cryoscopic constants (K_f) for common solvents used for cryoscopy.

2.2.3.3 Cryoscopic Method

The detailed information about the procedure used for cryoscopy is shown below:

- Step 1. Weigh (15 to 20 grams) of the pure solvent in a test tube and record the measured weight value of the pure solvent.
- Step 2. Place a stir bar or wire stirrer in the test tube and close with a rubber stopper that has a hole to encase a mercury thermometer.
- Step 3. Place a mercury thermometer in the rubber stopper hole.
- Step 4. Immerse the test tube apparatus in an ice-water bath.
- Step 5. Allow the solvent to stir continuously and equilibrate to a few degrees below the freezing point of the solvent.
- Step 6. Record the temperature at which the solvent reaches the freezing point, which remains at a constant temperature reading.
- Step 7. Repeat the freezing point data collection for at least two more measurements without a difference less than 0.5 °C between the measurements.
- Step 8. Weigh a quantity of the solute for investigation and record the measured value.
- Step 9. Add the weighed solute to the test tube containing the pure solvent.
- Step 10. Re - close the test tube with a rubber stopper encasing a mercury thermometer.
- Step 11. Re-immerses the test tube in an ice water bath and allow the mixture to stir to fully dissolve the solute in the pure solvent.
- Step 12. Measure the freezing point and record the temperature value.

NOTE: Allow the solution to stir continuously to avoid supercooling.

The observed freezing point of the solution is when the temperature reading remains constant.

2.2.4 Sample calculation to determine molecular weight

2.2.4.1 Sample data set

Table 2.2 represents an example of a data set collection for cryoscopy.

Parameter	Trial 1	Trial 2	Trial 3	Avg
Mass of cyclohexane (g)	9.05	9.00	9.04	9.03
Mass of unknown solute (g)	0.4000	0.4101	0.4050	0.4050
Freezing point of cyclohexane (°C)	6.5 °C	6.5 °C	6.5 °C	6.5 °C .
Freezing point of cyclohexane mixed with unknown solute (°C)	4.2 °C	4.3 °C	4.2 °C	4.2 °C

Table 2.2: Example of a data set collection for cryoscopy

2.2.4.2 Calculation of molecular weight using the freezing point depression equation

Calculate the freezing point (Fpt) depression of the solution,

$T\Delta_f$ (from Table 2.2).

$$T\Delta_f = (\text{Fpt of pure solvent}) - (\text{Fpt of solution}) \quad (2.3)$$

$$T\Delta_f = 6.5\text{ °C} - 4.2\text{ °C} \quad (2.4)$$

$$T\Delta_f = 2.3\text{ °C} \quad (2.5)$$

Calculate the molal concentration, m , of the solution using the freezing point depression and K_f (see Table 2.1 and Table 2.2).

$$T\Delta_f = K_fm \quad (2.6)$$

$$m = (2.3\text{ °C})/(20.2\text{ °C/molal}) \quad (2.7)$$

$$m = 0.113\text{ molal} \quad (2.8)$$

NOTE: $m = \text{g (solute)}/\text{kg (solvent)}$

Calculate the M_W of the unknown sample.

NOTE: $i = 1$ for covalent compounds in (2.2).

$$M_W = \frac{K_f (\text{g solute})}{\Delta T_f (\text{kg solvent})} \quad (2.9)$$

$$M_W = \frac{20.2\text{ }^{\circ}\text{C}\cdot\text{kg}/\text{moles} \times 0.405\text{ g}}{2.3\text{ }^{\circ}\text{C} \times 0.00903\text{ kg}} \quad (2.10)$$

$$M_W = 393\text{ g/mol} \quad (2.11)$$

Exercise 2.2.1 **(Solution on p. 211.)**

Nicotine Figure 2.9 is an extracted pale yellow oil from tobacco leaves that dissolves in water at temperatures less than 60 °C. What is the molality of nicotine in an aqueous solution that begins to freeze at -0.445 °C? See Table 2.1 for K_f values.

Exercise 2.2.2 **(Solution on p. 211.)**

If the solution used in Exercise 2.2.1 is obtained by dissolving 1.200 g of nicotine in 30.56 g of water, what is the molar mass of nicotine?

Exercise 2.2.3 **(Solution on p. 211.)**

What would be the freezing point depression when 0.500 molal of $\text{Ca}(\text{NO}_3)_2$ is dissolved in 60 g of water?

Exercise 2.2.4 **(Solution on p. 211.)**

Calculate the number of weighed grams of $\text{Ca}(\text{NO}_3)_2$ added to the 60 g of water to achieve the freezing point depression from Exercise 2.2.3? The M_W of $\text{Ca}(\text{NO}_3)_2$ is 164.088 g/moles.

2.2.5 Bibliography

- *Knovel Critical Tables*, 2nd Ed., Knovel, New York (2008).
- <http://www.lahc.cc.ca.us/classes/chemistry/arias/Exp%2012%20-%20Freezing%20Point.pdf>
- H. C. Jones, *The Modern Theory of Solutions: Memoirs by Pfeffer, Van't Hoff, Arrhenius, and Raoult*, Harper and Brothers, New York (1899).
- E. Beckmann, *Z. Anorg. Allg. Chem.*, 1910, **67**, 17.
- H. P. Ronningsen. *Energ. Fuel.*, 1993, **7**, 565.
- D. A McQuarrie, P. A Rock, and E. B. Gallogly, *General Chemistry*, University Science Books, Mill Valley (2011).

2.3 Molecular Weight of Polymers ⁶

2.3.1 Introduction

Knowledge of the molecular weight of polymers is very important because the physical properties of macromolecules are affected by their molecular weight. For example, shown in Figure 2.10 the interrelation between molecular weight and strength for a typical polymer.

⁶This content is available online at <<http://cnx.org/content/m43550/1.1/>>.

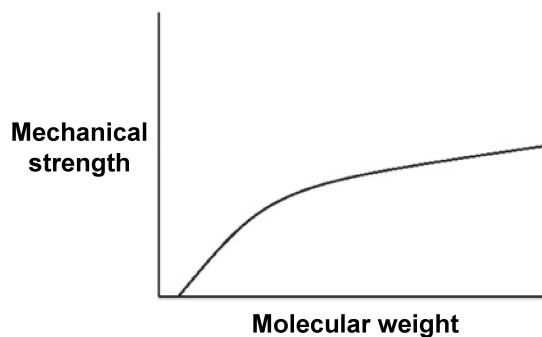


Figure 2.10: Dependence of mechanical strength on polymer molecular weight. Adapted from G. Odian, *Principles of Polymerization*, 4th edition, Wiley-Interscience, New York (2004).

The melting point of polymers are also slightly depend on their molecular weight. (Figure 2.11) shows relationship between molecular weight and melting temperatures of polyethylene (Figure 2.12). Most linear polyethylenes have melting temperatures near 140 °C. The approach to the theoretical asymptote, that is a line whose distance to a given curve tends to zero, indicative that a theoretical polyethylene of infinite molecular weight (i.e., $M = \infty$) would have a melting point of 145 °C.

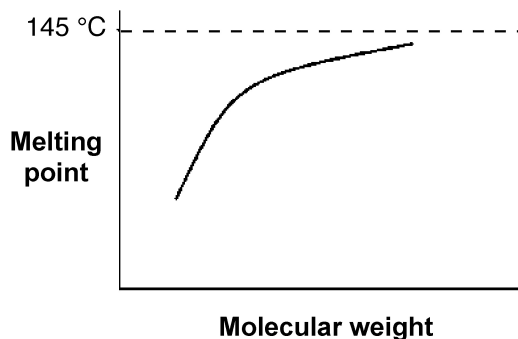


Figure 2.11: The molecular weight-melting temperature relationship for the alkane series. Adapted from L. H. Sperling, *Introduction to physical polymer science*, 4th edition, Wiley-Interscience, New York (2005).

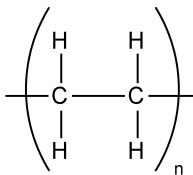


Figure 2.12: Structure of polyethylene.

There are several ways to calculate molecular weight of polymers like number average of molecular weight, weight average of molecular weight, Z-average molecular weight, viscosity average molecular weight, and distribution of molecular weight.

2.3.2 Molecular weight of polymers

2.3.2.1 Number average of molecular weight (M_n)

Number average of molecular weight is measured to determine number of particles. Number average of molecular weight is the total weight of polymer, (2.12), divided by the number of polymer molecules, (2.13). The number average molecular weight (M_n) is given by (2.14), where M_i is molecular weight of a molecule of oligomer n , and N_i is number of molecules of that molecular weight.

$$\text{Total weight} = \sum_{i=1}^{\infty} M_i N_i \quad (2.12)$$

$$\text{Total number} = \sum_{i=1}^{\infty} N_i \quad (2.13)$$

$$M_n = \frac{\sum M_i N_i}{\sum N_i} \quad (2.14)$$

Example 2.1

Consider a polymer sample comprising of 5 moles of polymer molecules having molecular weight of 40.000 g/mol and 15 moles of polymer molecules having molecular weight of 30.000 g/mol.

$$\text{Total weight} = (5 \text{ mol} \times 40.00 \text{ g/mol}) + (15 \text{ mole} \times 30.00 \text{ g/mol}) = 650,000 \text{ g} \quad (2.15)$$

$$\text{Total number} = 5 \text{ mol} + 15 \text{ mol} = 20 \text{ mol} \quad (2.16)$$

$$M_n = \frac{650,000 \text{ g}}{20 \text{ mol}} = 325,000 \text{ g/mol} \quad (2.17)$$

2.3.2.2 Weight average of molecular weight (M_w)

Weight average of molecular weight (M_w) is measured to determine the mass of particles. M_w defined as (2.18), where M_i is molecular weight of a molecule of oligomer n , and N_i is number of molecules of that molecular weight.

$$M_w = \frac{\sum N_i (M_i)^2}{\sum N_i M_i} \quad (2.18)$$

Example 2.2

Consider the polymer described in Example 2.1.

$$M_w = \frac{(5 \text{ mol} \times (40,000 \text{ g/mol})^2) + (15 \text{ mol} \times (30,000 \text{ g/mol})^2)}{(5 \text{ mol} \times 40,000 \text{ g/mol}) + (15 \text{ mol} \times 30,000 \text{ g/mol})} \quad (2.19)$$

$$M_w = 330,769 \text{ g/mol} \quad (2.20)$$

Exercise 2.3.1

(Solution on p. 211.)

Calculate the M_w for a polymer sample comprising of 9 moles of polymer molecules having molecular weight of 30,000 g/mol and 5 moles of polymer molecules having molecular weight of 50,000 g/mol.

2.3.2.3 Z-average molecular weight (M_z)

The Z-average molecular weight (M_z) is measured in some sedimentation equilibrium experiments. M_z isn't common technique for molecular weight of polymers. The molar mass depends on size and mass of the molecules. The ultra centrifugation techniques employ to determine M_z . M_z emphasizes large particles and it defines the EQ, where M_i is molecular weight and N_i is number of molecules.

$$M_z = \frac{\sum N_i M_i^3}{\sum N_i M_i^2} \quad (2.21)$$

Example 2.3

Consider the polymer described in Example 2.1.

$$M_z = \frac{(5 \text{ mol} \times (40,000 \text{ g/mol})^3) + (15 \text{ mol} \times (30,000 \text{ g/mol})^3)}{(5 \text{ mol} \times (40,000 \text{ g/mol})^2) + (15 \text{ mol} \times (30,000 \text{ g/mol})^2)} \quad (2.22)$$

$$M_z = \frac{7.25 \times 10^{14} \text{ g}^3/\text{mol}^4}{2.15 \times 10^{10} \text{ g}^2/\text{mol}^3} \quad (2.23)$$

$$M_z = 337,209 \text{ g/mol} \quad (2.24)$$

Exercise 2.3.2

(Solution on p. 211.)

Calculate the M_z for a polymer sample comprising of 10 moles of polymer molecules having molecular weight of 20,000 g/mol and 2 moles of polymer molecules having molecular weight of 25,000 g/mol.

2.3.2.4 Viscosity average molecular weight (M_v)

One of the ways to measure the average molecular weight of polymers is viscosity of solution. Viscosity of a polymer depend on concentration and molecular weight of polymers. Viscosity techniques is common since it is experimentally simple. Viscosity average molecular weight defines as (2.25), where M_i is molecular weight and N_i is number of molecules, a is a constant which depend on the polymer-solvent in the viscosity experiments. When a is equal 1, M_v is equal to the weight average molecular weight, if it isn't equal 1 it is between weight average molecular weight and the number average molecular weight.

$$M_v = \left(\frac{\sum N_i M_i^{1+a}}{\sum N_i M_i} \right)^{1/2} \quad (2.25)$$

2.3.2.5 Distribution of molecular weight

Molecular weight distribution is one of the important characteristic of polymer because it affects polymer properties. A typical molecular distribution of polymers show in Figure 2.13.. There are various molecular weight in the range of curve. The distribution of sizes in a polymer sample isn't totally defined by its central tendency. The width and shape of distribution must be known. It is always true that the various range molecular weight is (2.26). The equality is occurring when all polymer in the sample have the same molecular weight.

$$M_N \leq M_v \leq M_w \leq M_z \leq M_{z+1} \quad (2.26)$$

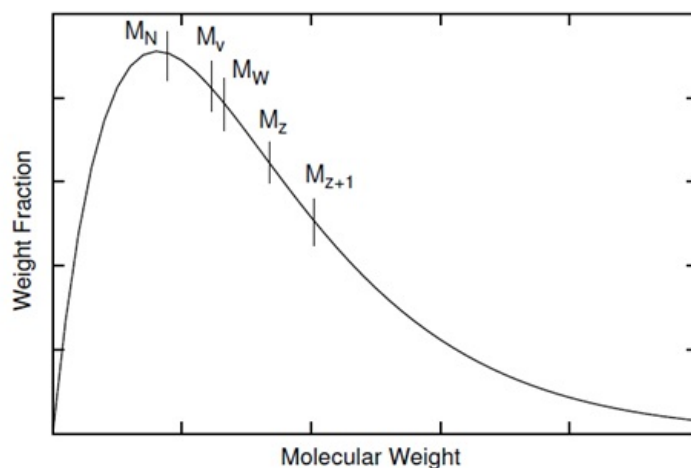


Figure 2.13: A schematic plot of a distribution of molecular weights along with the rankings of the various average molecular weights. Adapted from J. A. Nairn, Oregon State University (2003).

2.3.3 Molecular weight analysis of polymers

2.3.3.1 Gel permeation chromatography (GPC)

Gel permeation chromatography is also called size exclusion chromatography. It is widely used method to determine high molecular weight distribution. In this technique, substances separate according to their molecule size. Firstly, large molecules begin to elute then smaller molecules are eluted Figure 2.14. The sample is injected into the mobile phase then the mobile phase enters into the columns. Retention time is the length of time that a particular fraction remains in the column. As shown in Figure 2.14, while the mobile phase passes through the porous particles, the area between large molecules and small molecules is getting increase. GPC gives a full molecular distribution, but its cost is high.

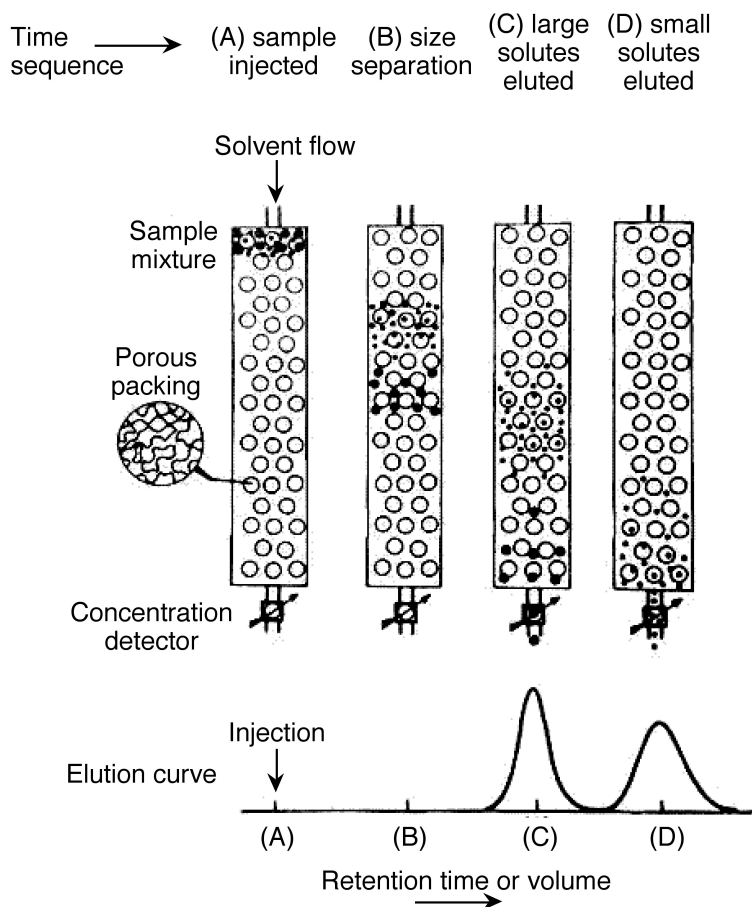


Figure 2.14: Solvent flow through column. Adapted from A. M. Striegel, W. W. Yau, J. J. Kirkland, and D. D. Bly. *Modern Size-Exclusion Liquid Chromatography- Practice of Gel Permeation and Gel Filtration Chromatography*, 2nd Edition. Hoboken. N.J. (2009).

According to basic theory of GPC, the basic quantity measured in chromatography is the retention volume, (2.27), where V_0 is mobile phase volume and V_p is the volume of a stationary phase. K is a

distribution coefficient related to the size and types of the molecules.

$$V_e = V_0 + V_p K \quad (2.27)$$

The essential features of gel permeation chromatography are shown in Figure 2.15. Solvent leaves the solvent supply, then solvent is pumped through a filter. The desired amount of flow through the sample column is adjusted by sample control valves and the reference flow is adjusted that the flow through the reference and flow through the sample column reach the dedector in common front. The reference column is used to remove any slight impurities in the solvent. In order to determine the amount of sample, a detector is located at the end of the column. Also, detectors may be used to continuously verify the molecular weight of species eluting from the column. The flow of solvent volume is as well monitored to provide a means of characterizing the molecular size of the eluting species.

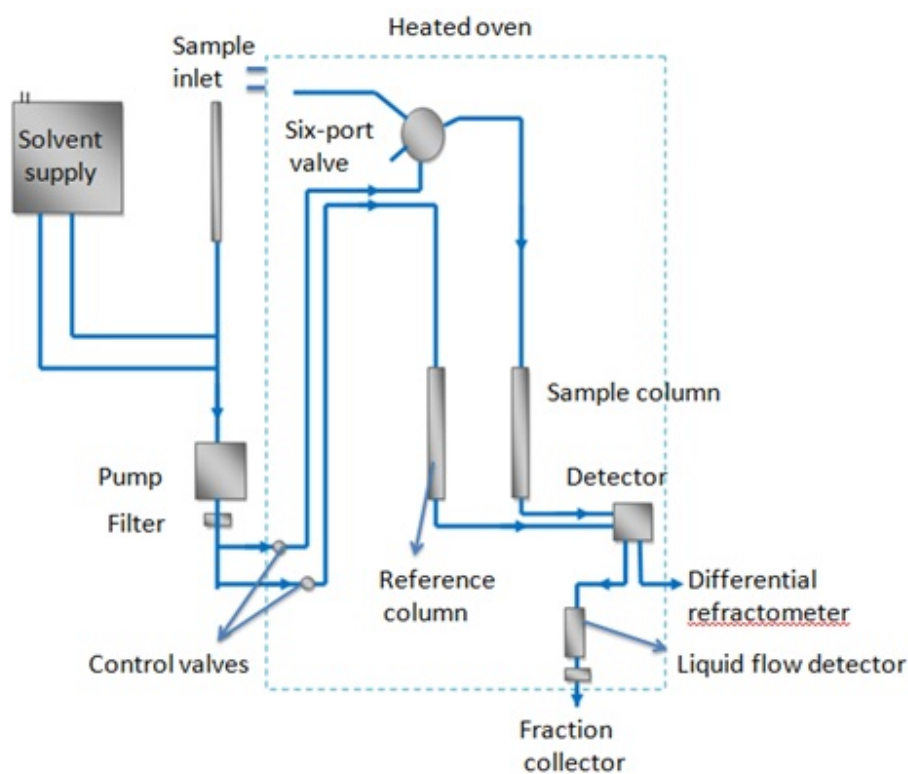


Figure 2.15: Schematic of gel permeation chromatography system.

As an example, consider the block copolymer of ethylene glycol (PEG, Figure 2.19) and poly(lactide) (PLA, Figure 2.17), i.e., Figure 2.18. In the first step starting with a sample of PEG with a M_n of 5,700 g/mol. After polymerization, the molecular weight increased because of the progress of lactide polymerization initiated from end of PEG chain. Varying composition of PEG-PLA shown in Table 2.3 can be detected by GPC (Figure 2.19).

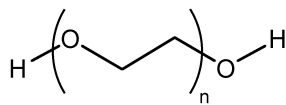


Figure 2.16: The structure of polyethyleneglycol (PEG).

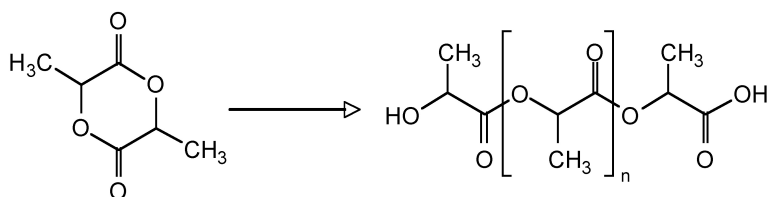


Figure 2.17: The ring-opening polymerization of lactide to polylactide.

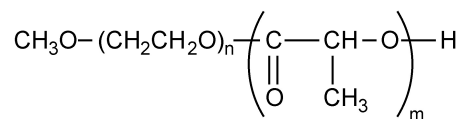


Figure 2.18: The structure of PEG-PLA block copolymer.

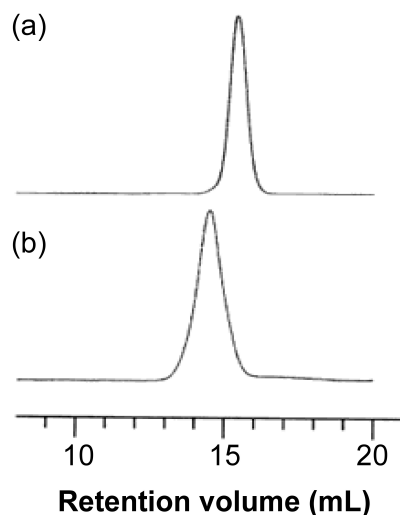


Figure 2.19: Gel permeation chromatogram of (a) PEG ($M_w = 5,700$ g/mol) and (b) PEG-PLA block copolymer ($M_w = 11,000$ g/mol). Adapted from K. Yasugi, Y. Nagasaki, M. Kato, K. Kataoka, *J. Control. Release*, 1999, **62**, 89.

Polymer	M_n of PEG	M_w/M_n of PEG	M_n of PLA	M_w/M_n of block copolymer	Weight ratio of PLA to PEG
PEG-PLA(41-12)	4100	1.05	1200	1.05	0.29
PEG-PLA(60-30)	6000	1.03	3000	1.08	0.50
PEG-PLA(57-54)	5700	1.03	5400	1.08	0.95
PEG-PLA(61-78)	6100	1.03	7800	1.11	1.28

Table 2.3: Characteristics of PEG-PLA block copolymer with varying composition. Adapted from K. Yasugi, Y. Nagasaki, M. Kato, and K. Kataoka, *J. Control Release*, 1999, **62**, 89.

2.3.3.2 Light-scattering

One of the most used methods to characterize the molecular weight is light scattering method. When polarizable particles are placed in the oscillating electric field of a beam of light, the light scattering occurs. Light scattering method depends on the light, when the light is passing through polymer solution, it is measure by loses energy because of absorption, conversion to heat and scattering. The intensity of scattered light relies on the concentration, size and polarizability that is proportionality constant which depends on the molecular weight. Figure 2.20 shows light scattering off a particle in solution.

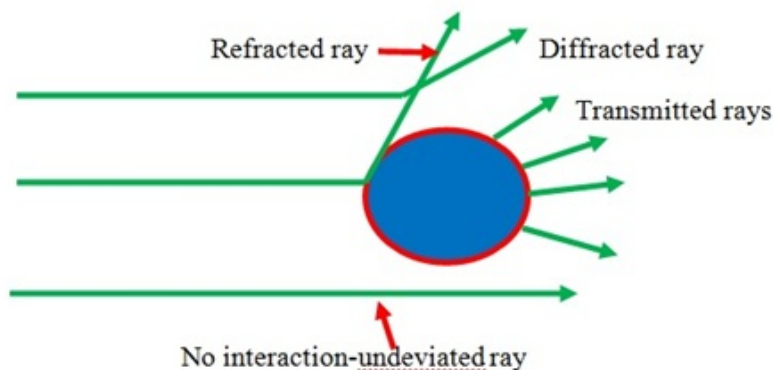


Figure 2.20: Modes of scattering of light in solution.

A schematic laser light-scattering is shown in Figure 2.21. A major problem of light scattering is to prepare perfectly clear solutions. This problem is usually accomplished by ultra-centrifugation. A solution should be as possible as clear and dust free to determine absolute molecular weight of polymer. The advantages of this method, it doesn't need calibration to obtain absolute molecular weight and it can give information about shape and M_w information. Also, it can be performed rapidly with less amount of sample and absolute determinations of the molecular weight can be measured. The weaknesses of the method is high price and most times it requires difficult clarification of the solutions.

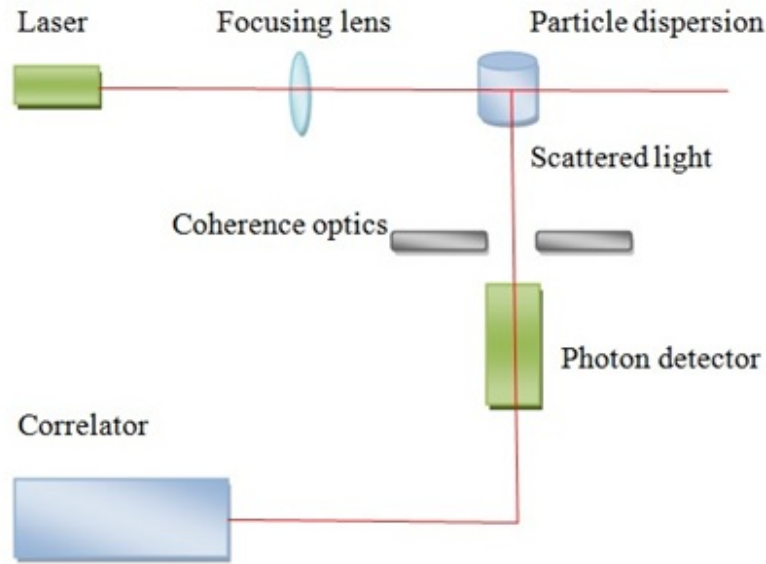


Figure 2.21: Schematic representation of light scattering. Adapted from J. A. Nairn, polymer characterization, *Material science and engineering* 5473, spring 2003.

The weight average molecular weight value of scattering polymers in solution related to their light scattering properties that define by (2.28), where K is the wave vector, that defined by (2.29). C is solution concentration, $R(\theta)$ is the reduced Rayleigh ratio, $P(\theta)$ the particle scattering function, θ is the scattering angle, A is the osmotic virial coefficients, where n_0 solvent refractive index, λ the light wavelength and N_a Avagadro's number. The particle scattering function is given by (2.30), where R_z is the radius of gyration.

$$KC/R(\theta) = 1/M_w(P(\theta) + 2A_2C + 3A_3C^2 + \dots) \quad (2.28)$$

$$K = 2\pi^2 n_0^2 (dn/dC)^2 / N_a \lambda^4 \quad (2.29)$$

$$1/P(\theta) = 1 + 16\pi^2 n_0^2 (R_z^2) \sin^2(\theta/2) / 3\lambda^2 \quad (2.30)$$

Weight average molecular weight of a polymer is found from extrapolation of data in the form of a Zimm plot (Figure 2.22). Experiments are performed at several angles and at least at 4 different concentrations. The straight line extrapolations provides M_w .

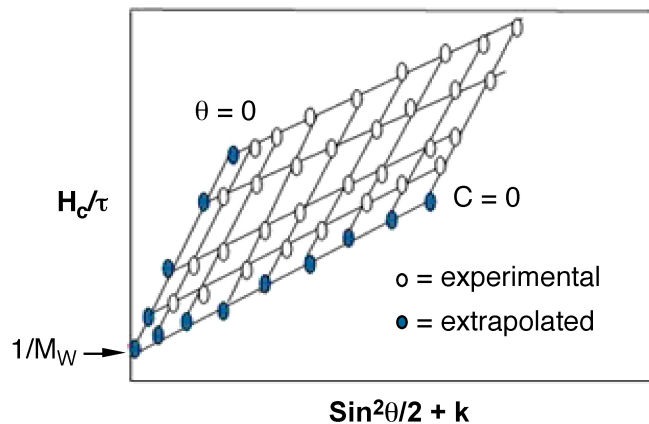


Figure 2.22: A typical Zimm plot of light scattering data. Adapted from M. P. Stevens, *Polymer Chemistry an Introduction*, 3rd edition, Oxford University Press, Oxford (1999).

2.3.3.3 X-ray scattering

X-rays are a form of electromagnetic wave with wavelengths between 0.001 nm and 0.2 nm. X-ray scattering is particularly used for semicrystalline polymers which includes thermoplastics, thermoplastic elastomers, and liquid crystalline polymers. Two types of X-ray scattering are used for polymer studies:

1. Wide-angle X-ray scattering (WAXS) which is used to study orientation of the crystals and the packing of the chains.
2. Small-angle X-ray scattering (SAXS) which is used to study the electron density fluctuations that occur over larger distances as a result of structural inhomogeneities.

Schematic representation of X-ray scattering shows in Figure 2.23.

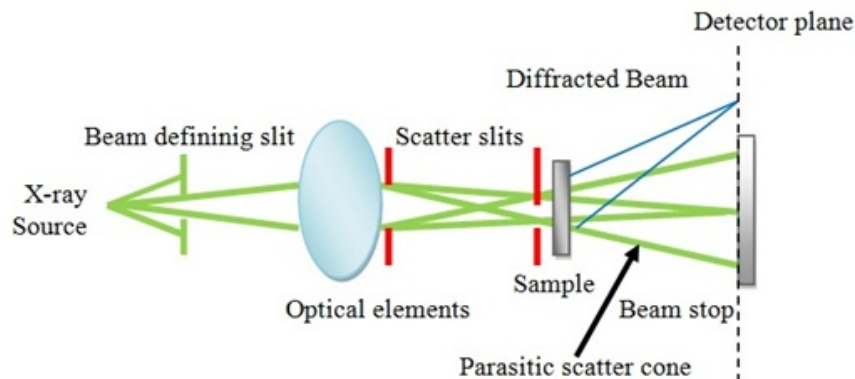


Figure 2.23: Schematic diagram of X-ray scattering. Adapted from B. Chu, and B. S. Hsiao, *Chem. Rev.* 2001,**101**, 1727.

At least two SAXS curves are required to determine the molecular weight of a polymer. The SAXS procedure to determine the molecular weight of polymer sample in monomeric or multimeric state solution requires the following conditions.

- The system should be monodispersed.
- The solution should be dilute enough to avoid spatial correlation effects.
- The solution should be isotropic.
- The polymer should be homogeneous.

2.3.3.4 Osmometer

Osmometry is applied to determine number average of molecular weight (M_n). There are two types of osmometer:

- Vapor pressure osmometry (VPO).
- Membrane osmometry.

Vapor pressure osmometry measures vapor pressure indirectly by measuring the change in temperature of a polymer solution on dilution by solvent vapor and is generally useful for polymers with M_n below 10,000–40,000 g/mol. When molecular weight is more than that limit, the quantity being measured becomes very small to detect. A typical vapor osmometry shows in the Figure 2.24. Vapor pressure is very sensitive because of this reason it is measured indirectly by using thermistors to measure voltage changes caused by changes in temperature.

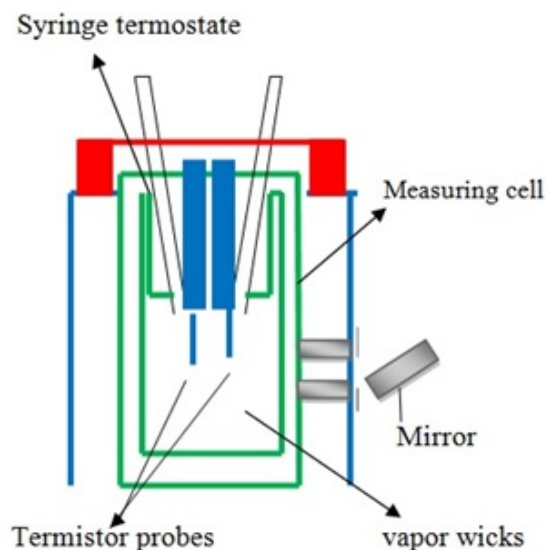


Figure 2.24: Schematic vapor pressure osmometry. Adapted from <http://www.gallay.com.au/node/186>⁷

Membrane osmometry is absolute technique to determine M_n (Figure 2.25). The solvent is separated from the polymer solution with semipermeable membrane that is strongly held between the two chambers. One chamber is sealed by a valve with a transducer attached to a thin stainless steel diaphragm which permits the measurement of pressure in the chamber continuously. Membrane osmometry is useful to determine M_n about 20,000-30,000 g/mol and less than 500,000 g/mol. When M_n of polymer sample more than 500,000 g/mol, the osmotic pressure of polymer solution becomes very small to measure absolute number average of molecular weight. In this technique, there are problems with membrane leakage and symmetry. The advantages of this technique is that it doesn't require calibration and it gives an absolute value of M_n for polymer samples.

⁷<http://www.gallay.com.au/node/186>

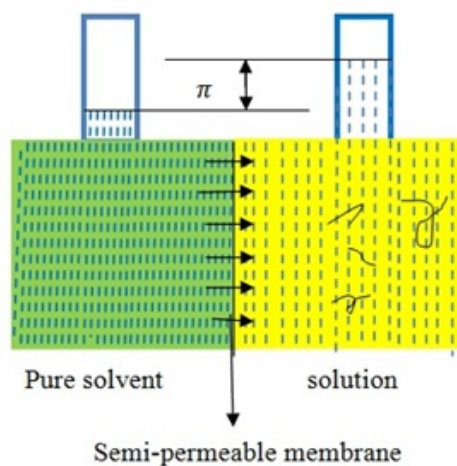


Figure 2.25: Schematic representative of membrane osmometry. Adapted from <http://www.flickr.com/photos/mitopencourseware/3327963527/>⁸.

2.3.4 Summary

Properties of polymers depend on their molecular weight. There are different kind of molecular weight and each can be measured by different techniques. The summary of these techniques and molecular weight is shown in the Table 2.4.

Method	Type of molecular weight	Range of application
Light scattering	M_w	∞
Membrane osmometry	M_n	10^4 - 10^6
Vapor phase osmometry	M_n	40,000
X-ray scattering	M_w, n, z	10^2 to

Table 2.4: Summary of techniques of molecular weight of polymers.

2.3.5 Bibliography

- G. Odian, *Principle of Polymerization*, 4th edition, Wiley Interscience, New York (2004).
- M. P. Stevens, *Polymer Chemistry an Introduction*, 3rd Edition, Oxford University Press, Oxford (1998).
- T. Tanaka, *Experimental Methods in Polymer Science*, Academic Press, New York (1999).

⁸<http://www.flickr.com/photos/mitopencourseware/3327963527/>

- L. H. Sperling, *Introduction to physical polymer science*, 4th edition, Wiley-Interscience, New York (2006).
- R. W. Nunes, J. R. Martin, and J. F. Johnson, *Poly. Eng. Sci.*, 1982, **22**, 4.
- A. Horta and M. A. Pastoriza, *J. Chem. Educ.*, 2007, **84**, 7.
- K. Yasugi, Y. Nagasaki, M. Kato, and K. Kataoka, *J. Control. Release*, 1999, **62**, 89.
- B. Chu and B. S. Hsiao, *Chem. Rev.*, 2001, **101**, 1727.
- V. E. Eskin, *Sov. Phys. Usp.*, 1964, **7**, 2.
- B. H. Bersted, *J. Appl. Polym. Sci.*, 1973, **17**, 1415.
- A. H. Compton, *Physics*, 1925, **11**, 303
- C. H. Hsu, P. M. Peacock, R. B. Flippen, S. K. Manohar, and A. G. MacDiarmid, *Synth. Met.*, 1993, **60**, 233.
- <http://www.gallay.com.au/node/186> ⁹
- <http://www.flickr.com/photos/mitopencourseware/3327963527/> ¹⁰

2.4 Size Exclusion Chromatography and its Application in Polymer Science ¹¹

2.4.1 Introduction

Size exclusion chromatography (SEC) is a useful technique that is specifically applicable to high-molecular-weight species, such as polymer. It is a method to sort molecules according to their sizes in solution. The sample solution is injected into the column, which is filled with rigid, porous, materials, and is carried by the solvent through the packed column. The sizes of molecules are determined by the pore size of the packing particle in the column within which the separation occurs.

For polymeric materials, the molecular weight (M_w) or molecular size plays a key role in determining the mechanical, bulk, and solution properties of materials. It is known that the sizes of polymeric molecules depend on their molecular weights, side chain configurations, molecular interaction, and so on. For example, the exclusion volume of polymers with rigid side group is larger than those with soft long side chains. Therefore, in order to determine the molecular weight and molecular weight distribution of a polymer, one of the most widely applied methods is gel-permeation chromatography.

NOTE: Gel permeation chromatography (GPC) is a term used for when the separation technique size exclusion chromatography (SEC) is applied to polymers.

The primary purpose and use of the SEC technique is to provide molecular weight distribution information about a particular polymeric material. Typically, in about 30 minutes using standard SEC, the complete molecular weight distribution of a polymer as well as all the statistical information of the distribution can be determined. Thus, SEC has been considered as a technique essentially supplanting classical molecular weight techniques. To apply this powerful technique, there is some basic work that needs to be done before its use. The selection of an appropriate solvent and the column, as well as the experimental conditions, are important for proper separation of a sample. Also, it is necessary to have calibration curves in order to determine the relative molecular weight from a given retention volume/time.

It is well known that both the majority of natural and synthetic polymers are polydispersed with respect to molar mass. For synthetic polymers, the more mono-dispersed a polymer can be made, the better the understanding of its inherent properties will be obtained.

⁹<http://www.gallay.com.au/node/186>

¹⁰<http://www.flickr.com/photos/mitopencourseware/3327963527/>

¹¹This content is available online at <<http://cnx.org/content/m34657/1.2/>>.

2.4.2 Polymer properties

A polymer is a large molecule (macromolecule) composed of repeating structural units typically connected by covalent chemical bonds. Polymers are common materials that are widely used in our lives. One of the most important features which distinguishes most synthetic polymers from simple molecular compounds is the inability to assign an exact molar mass to a polymer. This is a consequence of the fact that during the polymerization reaction the length of the chain formed is determined by several different events, each of which have different reaction rates. Hence, the product is a mixture of chains of different length due to the random nature of growth. In addition, some polymers are also branched (rather than linear) as a consequence of alternative reaction steps. The molecular weight (M_w) and molecular weight distribution influences many of the properties of polymers:

- **Processability** - the suitability of the polymer to physical processing.
- **Glass-transition temperature** - refers to the transformation of a glass-forming liquid into a glass.
- **Solution viscosity** - measure of the resistance of a fluid which is being deformed by either shear stress or tensile stress.
- **Hardness** - a measure of how resistant a polymer is to various kinds of permanent shape change when a force is applied.
- **Melt viscosity** - the rate of extrusion of thermoplastics through an orifice at a prescribed temperature and load.
- **Tear strength** - a measure of the polymers resistance to tearing.
- **Tensile strength** - as indicated by the maxima of a stress-strain curve and, in general, is the point when necking occurs upon stretching a sample.
- **Stress-crack resistance** - the formation of cracks in a polymer caused by relatively low tensile stress and environmental conditions.
- **Brittleness** - the liability of a polymer to fracture when subjected to stress.
- **Impact resistance** - the relative susceptibility of polymers to fracture under stresses applied at high speeds.
- **Flex life** - the number of cycles required to produce a specified failure in a specimen flexed in a prescribed manner.
- **Stress relaxation** - describes how polymers relieve stress under constant strain.
- **Toughness** - the resistance to fracture of a polymer when stressed.
- **Creep strain** - the tendency of a polymer to slowly move or deform permanently under the influence of stresses.
- **Drawability** - The ability of fiber-forming polymers to undergo several hundred percent permanent deformation, under load, at ambient or elevated temperatures.
- **Compression** - the result of the subjection of a polymer to compressive stress.
- **Fatigue** - the failure by repeated stress.
- **Tackiness** - the property of a polymer being adhesive or gummy to the touch.
- **Wear** - the erosion of material from the polymer by the action of another surface.
- **Gas permeability** - the permeability of gas through the polymer.

Consequently, it is important to understand how to determine the molecular weight and molecular weight distribution.

2.4.2.1 Molecular weight

Simpler pure compounds contain the same molecular composition for the same species. For example, the molecular weight of any sample of styrene will be the same (104.16 g/mol). In contrast, most polymers are not composed of identical molecules. The molecular weight of a polymer is determined by the chemical structure of the monomer units, the lengths of the chains and the extent to which the chains are interconnected to form branched molecules. Because virtually all polymers are mixtures of many large molecules, we have to resort to averages to describe polymer molecular weight.

The polymers produced in polymerization reactions have lengths which are distributed according to a probability function which is governed by the polymerization reaction. To define a particular polymer weight average, the average molecular weight M_{avg} is defined by (2.31). Where N_i is the number of molecules with molecular weight M_i .

$$M_{\text{avg}} = \frac{\sum N_i M_i^a}{\sum N_i M_i^{a-1}} \quad (2.31)$$

There are several possible ways of reporting polymer molecular weight. Three commonly used molecular weight descriptions are: the number average (M_n), weight average (M_w), and z-average molecular weight (M_z). All of three are applicable to different constant a in (2.31) and are shown in Figure 2.26.

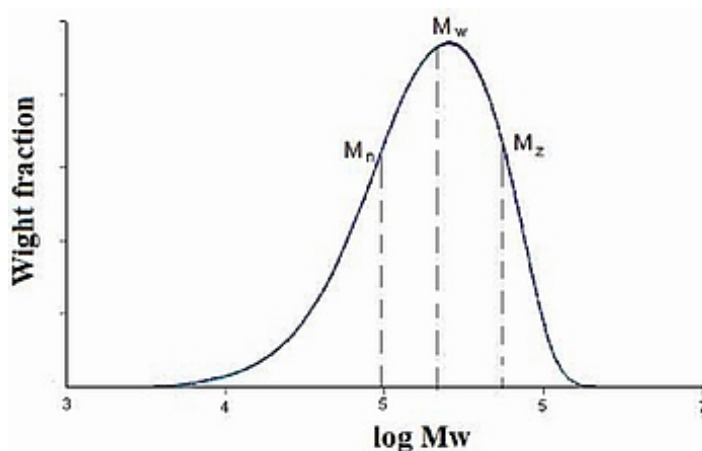


Figure 2.26: Distribution of molar masses for a polymer sample.

When $a = 1$, the number average molecular weight, (2.32).

$$M_{n,\text{avg}} = \frac{\sum N_i M_i}{\sum N_i} = \frac{w}{N} \quad (2.32)$$

When $a = 2$, the weight average molecular weight, (2.33).

$$M_{w,\text{avg}} = \frac{\sum N_i M_i^2}{\sum N_i M_i} = \frac{\sum N_i M_i^2}{w} \quad (2.33)$$

When $a = 3$, the z-average average molecular weight, (2.34).

$$M_{z,\text{avg}} = \frac{\sum N_i M_i^3}{\sum N_i M_i^2} = \frac{\sum N_i M_i^3}{\sum N_i M_i^2} \quad (2.34)$$

Bulk properties weight average molecular weight, M_w is the most useful one, because it fairly accounts for the contributions of different sized chains to the overall behavior of the polymer, and correlates best with most of the physical properties of interest.

There are various methods published to detect these three different primary average molecular weights respectively. For instance, a colligative method, such as osmotic pressure, effectively calculates the number of molecules present and provides a number average molecular weight regardless of their shape or size of polymers. The classical van't Hoff equation for the osmotic pressure of an ideal, dilute solution is shown in (2.35).

$$\frac{\pi}{c} = \frac{RT}{M_n} \quad (2.35)$$

The weight average molecular weight of a polymer in solution can be determined by either measuring the intensity of light scattered by the solution or studying the sedimentation of the solute in an ultracentrifuge. From light scattering method which is depending on the size rather than the number of molecules, weight average molecular weight is obtained. This work requires concentration fluctuations which are the main source of the light scattered by a polymer solution. The intensity of the light scattering of polymer solution is often expressed by its turbidity τ which is given in *Rayleigh's law* in (2.36). Where i_θ is scattered intensity at only one angle θ , r is the distance from the scattering particle to the detection point, and I_0 is the incident intensity.

$$\tau = \frac{16\pi i_\theta r^2}{3I_0(1+\cos^2\theta)} \quad (2.36)$$

The intensity scattered by molecules (N_i) of molecular weight (M_i) is proportional to $N_i M_i^2$. Thus, the total light scattered by all molecules is described in (2.37), where c is the total weight of the sample $\sum N_i M_i$.

$$\frac{\pi}{c} \sim \frac{\sum N_i M_i^2}{\sum N_i M_i} = M_{w,avg} \quad (2.37)$$

2.4.2.2 Poly-disperse index (PDI)

The polydispersity index (PDI), is a measure of the distribution of molecular mass in a given polymer sample. As shown in Figure 2.26, it is the result of the definitions that $M_w \geq M_n$. The equality of M_w and M_n would correspond with a perfectly uniform (monodisperse) sample. The ratio of these average molecular weights is often used as a guide to the dispersity of the chain lengths in a polymer sample. The greater M_w / M_n is, the greater the dispersity is.

The properties of a polymer sample are strongly dependent on the way in which the weights of the individual molecules are distributed about the average. The ratio M_w/M_n gives sufficient information to characterize the distribution when the mathematical form of the distribution curve is known.

Generally, the narrow molecular weight distribution materials are the models for much of work aimed at understanding the materials' behaviors. For example, polystyrene and its block copolymer polystyrene-b-polyisoprene have quite narrow distribution. As a result, narrow molecular weight distribution materials are a necessary requirement when people study their behavior, such as self-assembly behavior for block copolymer. Nonetheless, there are still lots of questions for scientists to explore the influence of polydispersity. For example, research on self-assembly which is one of the interesting fields in polymer science shows that we cannot throw polydispersity away.

2.4.3 Setup of SEC equipment

In SEC, sample components migrate through the column at different velocities and elute separately from the column at different times. In liquid chromatography and gas chromatography, as a solute moves along with

the carrier fluid, it is at times held back either by surface of the column packing, by stationary phase, or by both. Unlike gas chromatography (GC) and liquid chromatography (LC), molecular size, or more precisely, molecular hydrodynamic volume governs the separation process of SEC, not varied by the type of mobile phase. The smallest molecules are able to penetrate deeply into pores whereas the largest molecules are excluded by the smaller pore sizes. Figure 2.27 shows the regular instrumental setup of SEC.

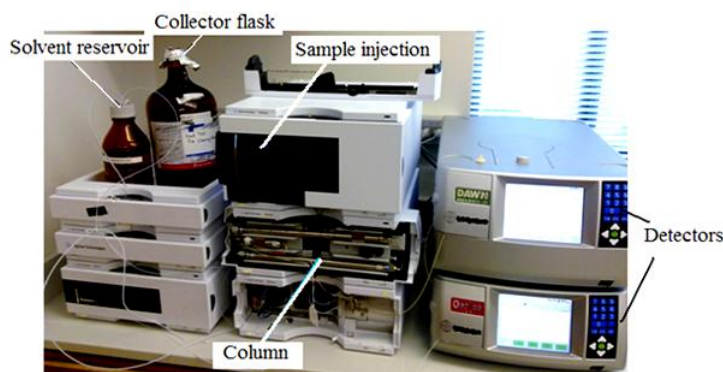


Figure 2.27: Regular instrumentation for size exclusion chromatography (SEC).

The properties of mobile phase are still important in that it is supposed to be strong affinity to stationary phase and be a good solubility to samples. The purpose of well soluble of sample is to make the polymer be perfect coil suspending in solution. Thus, as a mixture of solutes of different size passes through a column packed with porous particles. As shown in Figure 2.28, it clearly depicts the general idea for size separation by SEC. the main setup of SEC emphasizes three concepts: stationary phase (column), mobile phase (solvent) and sample preparation.

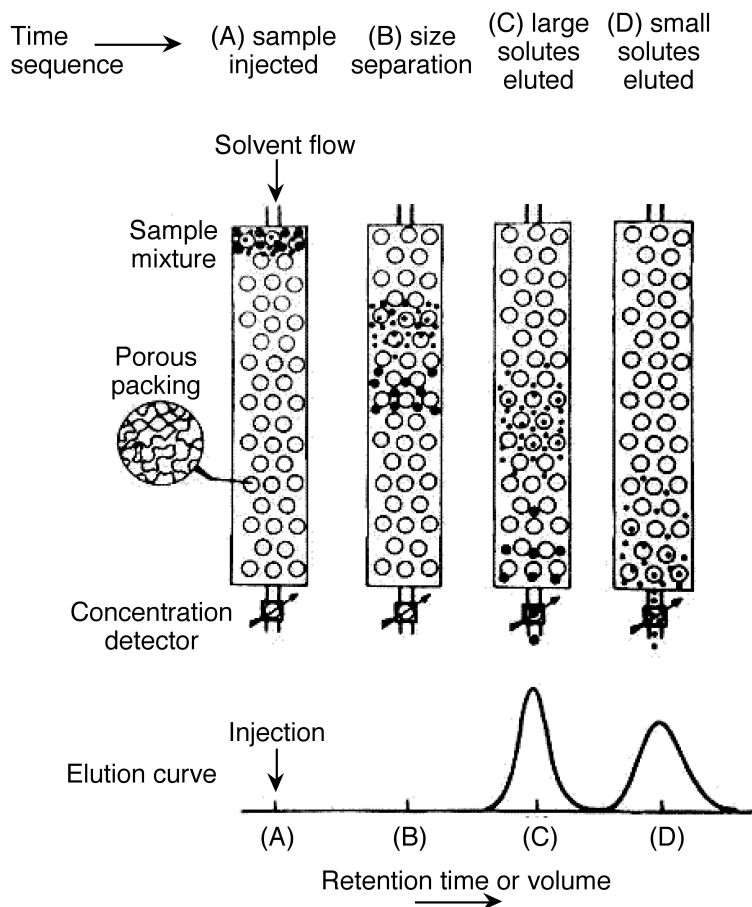


Figure 2.28: Development and detection of size separation by SEC. Adapted from A. M. Striegel, W. W. Yau, J. J. Kirkland, and D. D. Bly. *Modern Size-Exclusion Liquid Chromatography- Practice of Gel Permeation and Gel Filtration Chromatography*, 2nd Edition. Hoboken, N.J. (2009).

2.4.3.1 Solvent selection

Solvent selection for SEC involves a number of considerations, such as convenience, sample type, column packing, operating variables, safety, and purity.

For samples concern, the solvents used for mobile phase of SEC are limited to those follows following criteria:

- The solvent must dissolve the sample completely.
- The solvent has different properties with solute in the eluent: typically with solvent refractive index (RI) different from the sample RI by ± 0.05 unit of more, or more than 10% of incident energy for UV detector.
- The solvent must not degrade the sample during use. Otherwise, the viscosity of eluent will gradually increase over times.
- The solvent is not corrosive to any components of the equipment.

Therefore, several solvents are qualified to be solvents such as THF, chlorinated hydrocarbons (chloroform, methylene chloride, dichloroethane, etc), aromatic hydrocarbons (benzene, toluene, trichlorobenzene, etc).

Normally, high purity of solvent (HPLC-grade) is recommended. The reasons are to avoid suspended particulates that may abrade the solvent pumping system or cause plugging of small-particle columns, to avoid impurities that may generate baseline noise, and to avoid impurities that are concentrated due to evaporation of solvent.

2.4.3.2 Column selection

Column selection of SEC depends mainly on the desired molecular weight range of separation and the nature of the solvents and samples. Solute molecules should be separated solely by the size of gels without interaction of packing materials. Better column efficiencies and separations can be obtained with small particle packing in columns and high diffusion rates for sample solutes. Furthermore, optimal performance of an SEC packing materials involves high resolution and low column backpressure. Compatible solvent and column must be chosen because, for example, organic solvent is used to swell the organic column packing and used to dissolve and separate the samples.

It is convenient that columns are now usually available from manufacturers regarding the various types of samples. They provide the information such as maximum tolerant flow rates, backpressure tolerances, recommended sample concentration, and injection volumes, etc. Nonetheless, users have to notice a few things upon using columns:

- Vibration and extreme temperatures should be avoided because these will post irreversible damage on columns.
- For aqueous mobile phase, it is unwise to allow the extreme pH solutions staying in the columns for a long period of time.
- The columns should be stored with some neat organic mobile phase, or aqueous mobile phase with pH range 2 - 8 to prevent degradation of packing when not in use.

2.4.3.3 Sample preparation

The sample solutions are supposed to be prepared in dilute concentration (less than 2 mg/mL) for several concerns. For polymer samples, samples must be dissolved in the solvent same as used for mobile phase except some special cases. A good solvent can dissolve a sample in any proportion in a range of temperatures. It is a slow process for dissolution because the rate determining step is solvent diffusion into polymers to produce swollen gels. Then, gradual disintegration of gels makes sample-solvent mixture truly become solution. Agitation and warming the mixtures are useful methods to speed up sample preparation.

It is recommended to filter the sample solutions before injecting into columns or storing in sample vials in order to get rid of clogging and excessively high pressure problems. If unfortunately the excessively high pressure or clogging occur due to higher concentration of sample solution, raising the column temperature will reduce the viscosity of the mobile phase, and may be helpful to redissolve the precipitated or adsorbed solutes in the column. Back flushing of the columns should only be used as the last resort.

2.4.4 Analysis of SEC data

The size exclusion separation mechanism is based on the effective hydrodynamic volume of the molecule, not the molecular weight, and therefore the system must be calibrated using standards of known molecular weight and homogeneous chemical composition. Then, the curve of sample is used to compare with calibration curve and obtain information relative to standards. The further step is required to convert relative molecular weight into absolute molecular weight of a polymer.

2.4.4.1 Calibration

The purpose of calibration in SEC is to define the relationship between molecular weight and retention volume/time in the chosen permeation range of column set and to calculate the relative molecular weight to standard molecules. There are several calibration methods commonly employed in modern SEC: direct standard calibration, poly-disperse standard calibration, universal calibration.

The most commonly used calibration method is direct standard calibration. In the direct standard calibration method, narrowly distributed standards of the same polymer being analyzed are used. Normally, narrow-molecular weight standards commercially available are polystyrene (PS). The molecular weight of standards are measured originally by membrane osmometry for number-average molecular weight, and by light scattering for weight-average molecular weight as described above. The retention volume at the peak maximum of each standard is equated with its stated molecular weight.

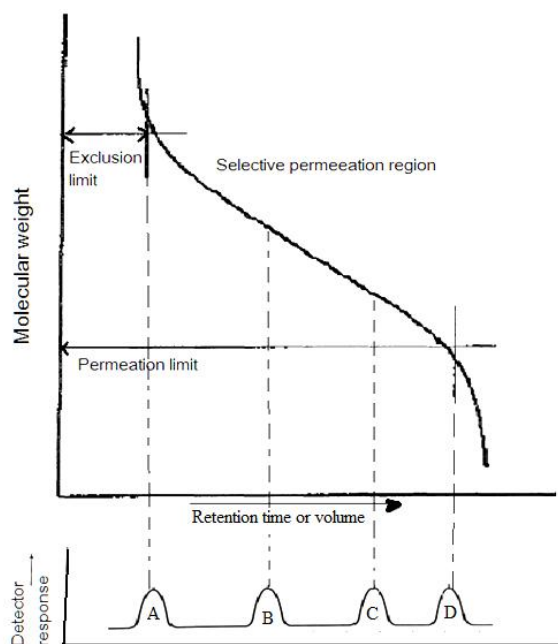


Figure 2.29: Calibration curve for a size-exclusion.

2.4.4.2 Relative M_w versus absolute M_w

The molecular weight and molecular weight distribution can be determined from the calibration curves as described above. But as the relationship between molecular weight and size depends on the type of polymer, the calibration curve depends on the polymer used, with the result that true molecular weight can only be obtained when the sample is the same type as calibration standards. As Figure 2.30 depicted, large deviations from the true molecular weight occur in the instance of branched samples because the molecular density of these is higher than in the linear chains.

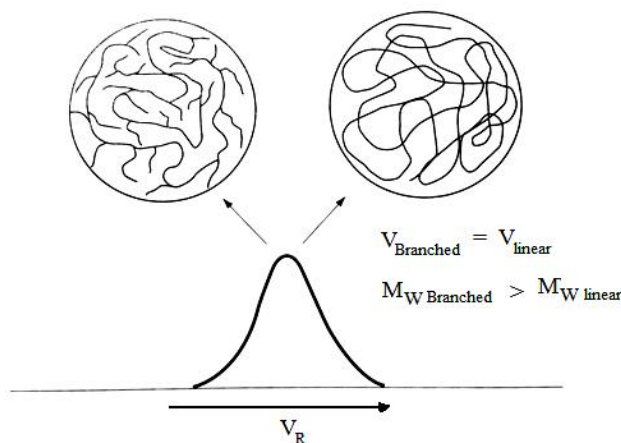


Figure 2.30: SEC elution of linear and branched samples of similar hydrodynamic volumes, but different molecular weights. S. Mori, and H. G. Barth. *Size Exclusion Chromatography*, Springer, New York. (1999).

Light-scattering detector is now often used to overcome the limitations of conventional SEC. These signals depend only on concentration, not on molecular weight or polymer size. For instance, for LS detector, (2.38) applies:

$$\text{LS signal} = K_{\text{LS}} \cdot (\text{dn/dc})^2 \cdot M_w \cdot c \quad (2.38)$$

Where K_{LS} is an apparatus-specific sensitivity constant, dn/dc is the refractive index increment and c is concentration. Therefore, accurate molecular weight can be determined while the concentration of the sample is known without calibration curve.

2.4.5 A practical example

The syntheses of poly(3-hexylthiophene) are well developed during last decade. It is an attractive polymer due to its potential as electronic materials. Due to its excellent charge transport performances and high solubility, several studies discuss its further improvement such as making block copolymer even triblock copolymer. The details are not discussed here. However, the importance of molecular weight and molecular weight distribution is still critical.

As shown in Figure 2.31, they studied the mechanism of chain-growth polymerization and successfully produced low polydispersity P3HT. The figure also demonstrates that the molecule with larger molecular size/ or weight elutes out of the column earlier than those which has smaller molecular weight.

The real molecular weight of P3HT is smaller than the molecular weight relative to polystyrene. In this case, the backbone of P3HT is harder compared with polystyrenes' backbone because of the position of aromatic groups. It results in less flexibility. We can briefly judge the authentic molecular weight of the synthetic polymer according to its molecular structure.

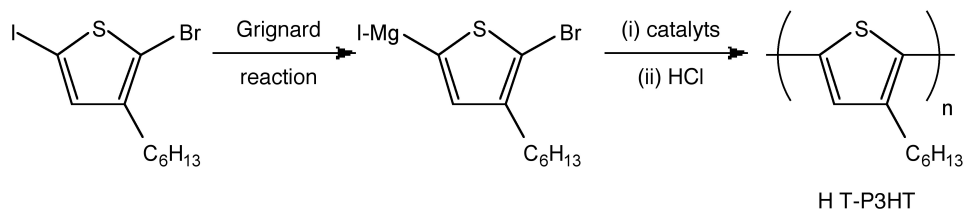


Figure 2.31: Synthesis of a well-defined poly(3-hexylthiophene) (HT-P3HT).

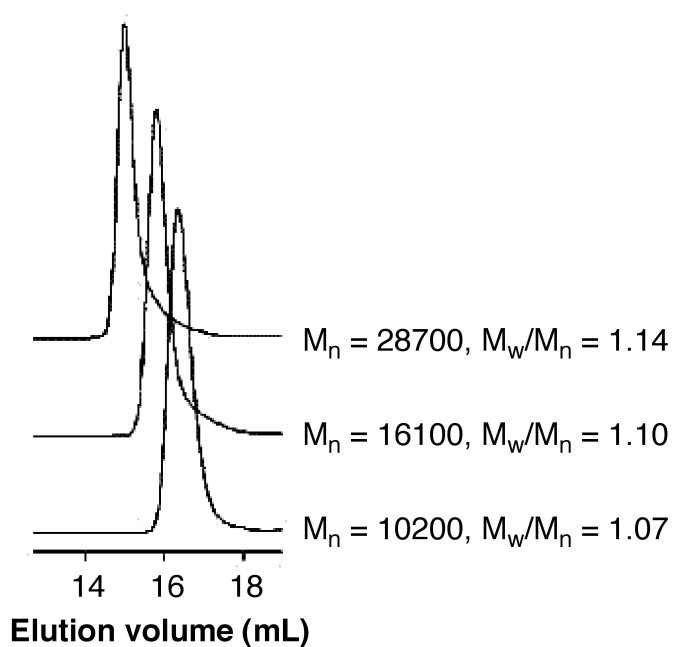


Figure 2.32: GPC profiles of HT-P3HT obtained by the polymerization. Adapted from R. Miyakoshi, A. Yokoyama, and T. Yokozawa, *Macromol. Rapid Commun.*, 2004, **25**, 1663.

2.4.6 Bibliography

- H. Allcock, and F. W. Lampe. *Contemporary Polymer Chemistry*, 2nd Edition, Englewood Cliffs, NJ (1990).
- J. M. G. Cowie, *Polymers: Chemistry and Physics of Modern Materials*, 3rd Edition. CRC Press (2007).
- P. J. Flory, *Principle of Polymer Chemistry*, Cornell University Press, Ithaca (1953).
- M. A. Hillmyer, *J. Polymer Sci. B: Polymer Phys.*, 2007, **45**, 3249.

- P. Meares, *Polymers: Structure and Bulk Properties*, Van Nostrand, New York (1971).
- J. Mitchell. *Applied Polymer Analysis and Characterization- Recent Developments in Techniques, Instrumentation, Problem Solving*, Verlag, Munich (1987).
- R. Miyakoshi, A. Yokoyama, and T. Yokozawa. *Macromol. Rapid Commun.*, 2004, **25**, 1663.
- R. Miyakoshi, A. Yokoyama, and T. Yokozawa, *J. Am. Chem. Soc.*, 2005, **127**, 17542.
- S. Mori, and H. G. Barth, *Size Exclusion Chromatography*, Springer, Berlin (1999).
- A. M. Striegel, W. W. Yau, J. J. Kirkland, and D. D. Bly. *Modern Size-Exclusion Liquid Chromatography-Practice of Gel Permeation and Gel Filtration Chromatography*, 2nd Edition, Hoboken, NJ (2009).

2.5 Thermogravimetric Analysis

2.5.1 Thermogravimetric Analysis of Single Walled Carbon Nanotubes¹²

Thermogravimetric analysis (TGA) and the associated differential thermal analysis (DTA) are widely used for the characterization of both as-synthesized and side-wall functionalized single walled carbon nanotubes (SWNTs). Under oxygen, SWNTs will pyrolyze leaving any inorganic residue behind. In contrast in an inert atmosphere since most functional groups are labile or decompose upon heating and as SWNTs are stable up to 1200 °C, any weight loss before 800 °C is used to determine the functionalization ratio of side-wall functionalized SWNTs. The following properties of SWNTs can be determined using this TGA;

1. The mass of metal catalyst impurity in as synthesized SWNTs.
2. The number of functional groups per SWNT carbon (C_{SWNT}).
3. The mass of a reactive species absorbed by a functional group on a SWNT.

Quantitative determination of these properties are used to define the purity of SWNTs, and the extent of their functionalization.

2.5.1.1 An overview of thermogravimetric analysis

The main function of TGA is the monitoring of the thermal stability of a material by recording the change in mass of the sample with respect to temperature. Figure 2.33 shows a simple diagram of the inside of a typical TGA.

¹²This content is available online at <<http://cnx.org/content/m22972/1.2/>>.

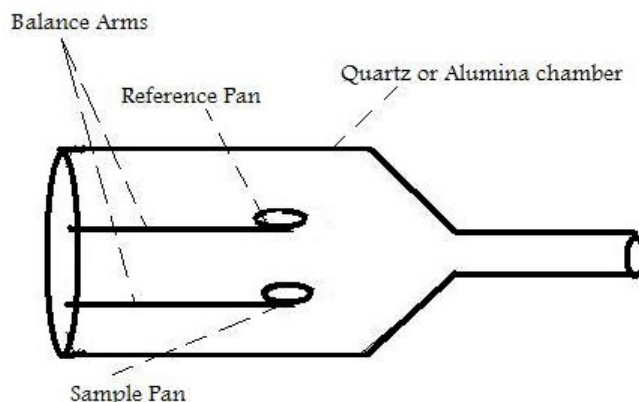


Figure 2.33: Schematic representation of a TGA apparatus.

Inside the TGA, there are two pans, a reference pan and a sample pan. The pan material can be either aluminium or platinum. The type of pan used depends on the maximum temperature of a given run. As platinum melts at $1760\text{ }^{\circ}\text{C}$ and aluminium melts at $660\text{ }^{\circ}\text{C}$, platinum pans are chosen when the maximum temperature exceeds $660\text{ }^{\circ}\text{C}$. Under each pan there is a thermocouple which reads the temperature of the pan. Before the start of each run, each pan is balanced on a balance arm. The balance arms should be calibrated to compensate for the differential thermal expansion between the arms. If the arms are not calibrated, the instrument will only record the temperature at which an event occurred and not the change in mass at a certain time. To calibrate the system, the empty pans are placed on the balance arms and the pans are weighed and zeroed.

As well as recording the change in mass, the heat flow into the sample pan (differential scanning calorimetry, DSC) can also be measured and the difference in temperature between the sample and reference pan (differential thermal analysis, DTA). DSC is quantitative and is a measure of the total energy of the system. This is used to monitor the energy released and absorbed during a chemical reaction for a changing temperature. The DTA shows if and how the sample phase changed. If the DTA is constant, this means that there was no phase change. Figure 2.34 shows a DTA with typical examples of an exotherm and an endotherm.

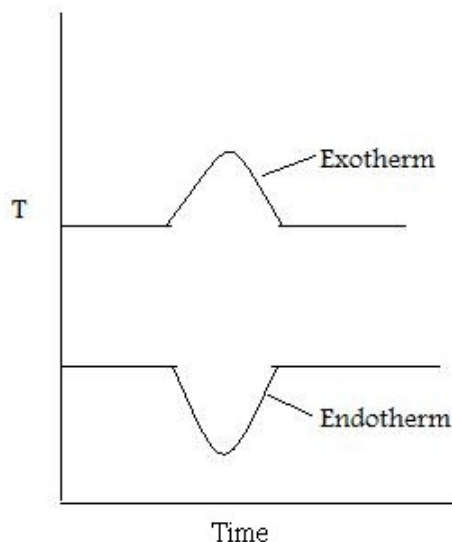


Figure 2.34: Simplified representation of the DTA for an exotherm and an endotherm.

When the sample melts, the DTA dips which signifies an endotherm. When the sample is melting it requires energy from the system. Therefore the temperature of the sample pan decreases compared with the temperature of the reference pan. When the sample has melted, the temperature of the sample pan increases as the sample is releasing energy. Finally the temperatures of the reference and sample pans equilibrate resulting in a constant DTA. When the sample evaporates, there is a peak in the DTA. This exotherm can be explained in the same way as the endotherm.

Typically the sample mass range should be between 0.1 to 10 mg and the heating rate should be 3 to 5 °C/min.

2.5.1.2 Determination of the mass of iron catalyst impurity in HiPCO SWNTs.

SWNTs are typically synthesized using metal catalysts. Those prepared using the HiPco method, contain residual Fe catalyst. The metal (i.e., Fe) is usually oxidized upon exposure to air to the appropriate oxide (i.e., Fe_2O_3). While it is sometimes unimportant that traces of metal oxide are present during subsequent applications it is often necessary to quantify their presence. This is particularly true if the SWNTs are to be used for cell studies since it has been shown that the catalyst residue is often responsible for observed cellular toxicity.

In order to calculate the mass of catalyst residue the SWNTs are pyrolyzed under air or O_2 , and the residue is assumed to be the oxide of the metal catalyst. Water can be added to the raw SWNTs, which enhances the low-temperature catalytic oxidation of carbon. A typical TGA plot of a sample of raw HiPco SWNTs is shown in Figure 2.35.

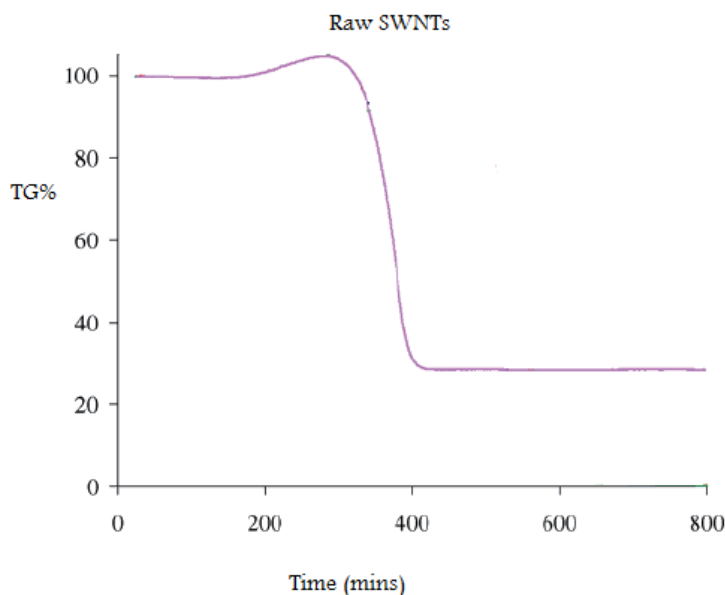


Figure 2.35: The TGA of unpurified HiPco SWNTs under air showing the residual mass associated with the iron catalyst. Adapted from I. W. Chiang, B. E. Brinson, A. Y. Huang, P. A. Willis, M. J. Bronikowski, J. L. Margrave, R. E. Smalley, and R. H. Hauge, *J. Phys. Chem. B*, 2001, **105**, 8297. Adapted from Chiang et al, 2001

The weight gain (of ca. 5%) at 300 °C is due to the formation of metal oxide from the incompletely oxidized catalyst. To determine the mass of iron catalyst impurity in the SWNT, the residual mass must be calculated. The residual mass is the mass that is left in the sample pan at the end of the experiment. From this TGA diagram, it is seen that 70% of the total mass is lost at 400 °C. This mass loss is attributed to the removal of carbon. The residual mass is 30%. Given that this is due to both oxide and oxidized metal, the original total mass of residual catalyst in raw HiPCO SWNTs is ca. 25%.

2.5.1.3 Determining the number of functional groups on SWNTs

The limitation of using SWNTs in any practical applications is their solubility; for example SWNTs have little to no solubility in most solvents due to aggregation of the tubes. Aggregation/roping of nanotubes occurs as a result of the high van der Waals binding energy of ca. 500 eV per μm of tube contact. The van der Waals force between the tubes is so great, that it takes tremendous energy to pry them apart, making it very difficult to make combination of nanotubes with other materials such as in composite applications. The functionalization of nanotubes, i.e., the attachment of “chemical functional groups”, provides the path to overcome these barriers. Functionalization can improve solubility as well as processability, and has been used to align the properties of nanotubes to those of other materials. In this regard, covalent functionalization provides a higher degree of fine-tuning for the chemical and physical properties of SWNTs than non-covalent functionalization.

Functionalized nanotubes can be characterized by a variety of techniques, such as atomic force microscopy (AFM), transmission electron microscopy (TEM), UV-vis spectroscopy, and Raman spectroscopy, however, the quantification of the extent of functionalization is important and can be determined using TGA. Because

any sample of functionalized-SWNTs will have individual tubes of different lengths (and diameters) it is impossible to determine the number of substituents per SWNT. Instead the extent of functionalization is expressed as number of substituents per SWNT carbon atom (C_{SWNT}), or more often as $C_{\text{SWNT}}/\text{substituent}$, since this is then represented as a number greater than 1.

Figure 2.36 shows a typical TGA for a functionalized SWNT. In this case it is polyethyleneimine (PEI) functionalized SWNTs prepared by the reaction of fluorinated SWNTs (F-SWNTs) with PEI in the presence of a base catalyst.

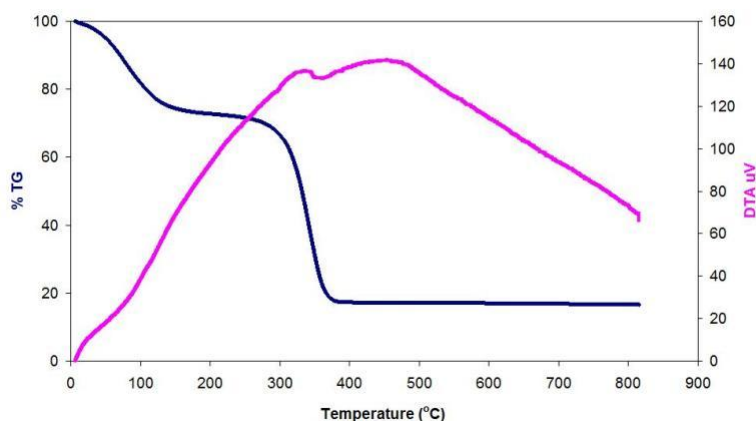


Figure 2.36: The TGA of SWNTs functionalized with polyethyleneimine (PEI) under air showing the sequential loss of complexed CO_2 and decomposition of PEI.

In the present case the molecular weight of the PEI is 600 g/mol. When the sample is heated, the PEI thermally decomposes leaving behind the unfunctionalized SWNTs. The initial mass loss below 100 °C is due to residual water and ethanol used to wash the sample.

In the following example the total mass of the sample is 25 mg.

- Step 1. The initial mass, $M_i = 25 \text{ mg} = \text{mass of the SWNTs, residues and the PEI}$.
- Step 2. After the initial moisture has evaporated there is 68% of the sample left. 68% of 25 mg is 17 mg. This is the mass of the PEI and the SWNTs.
- Step 3. At 300 °C the PEI starts to decompose and all of the PEI has been removed from the SWNTs at 370 °C. The mass loss during this time is 53% of the total mass of the sample. 53% of 25 mg is 13.25 mg.
- Step 4. The molecular weight of this PEI is 600 g/mol. Therefore there is $0.013 \text{ g} / 600 \text{ g/mol} = 0.022 \text{ mmole}$ of PEI in the sample.
- Step 5. 15% of the sample is the residual mass, this is the mass of the decomposed SWNTs. 15% of 25 mg is 3.75 mg. The molecular weight of carbon is 12 g/mol. So there is 0.3125 mmole of carbon in the sample.
- Step 6. There is 93.4 mol% of carbon and 6.5 mol% of PEI in the sample.

2.5.1.4 Determination of the mass of a chemical absorbed by functionalized SWNTs

Solid-state ^{13}C NMR of PEI-SWNTs shows the presence of carboxylate substituents that can be attributed to carbamate formation as a consequence of the reversible CO_2 absorption to the primary amine substituents

of the PEI. Desorption of CO₂ is accomplished by heating under argon at 75 °C.

The quantity of CO₂ absorbed per PEI-SWNT unit may be determined by initially exposing the PEI-SWNT to a CO₂ atmosphere to maximize absorption. The gas flow is switched to either Ar or N₂ and the sample heated to liberate the absorbed CO₂ without decomposing the PEI or the SWNTs. An example of the appropriate TGA plot is shown in Figure 2.37.

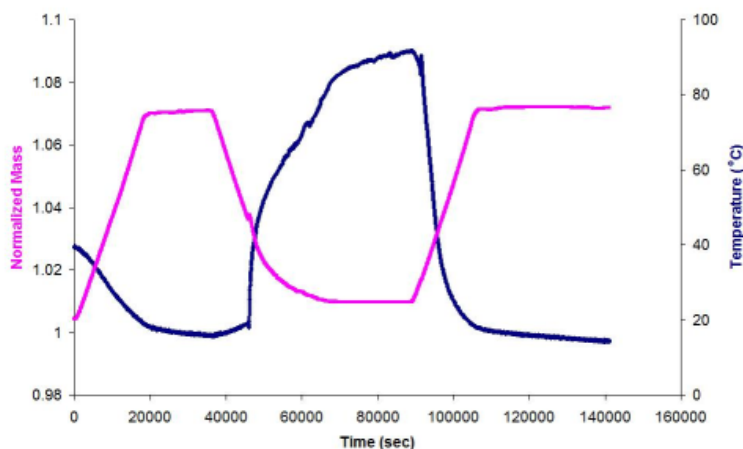


Figure 2.37: The TGA results of PEI(10000)-SWNT absorbing and desorbing CO₂. The mass has been normalized to the lowest mass recorded, which is equivalent to PEI(10000)-SWNT.

The sample was heated to 75 °C under Ar, and an initial mass loss due to moisture and/or atmospherically absorbed CO₂ is seen. In the temperature range of 25 °C to 75 °C the flow gas was switched from an inert gas to CO₂. In this region an increase in mass is seen, the increase is due to CO₂ absorption by the PEI (10000Da)-SWNT. Switching the carrier gas back to Ar resulted in the desorption of the CO₂.

The total normalized mass of CO₂ absorbed by the PEI(10000)-SWNT can be calculated as follows;

Solution Outline

- Step 1. Minimum mass = mass of absorbant = $M_{\text{absorbant}}$
- Step 2. Maximum mass = mass of absorbant and absorbed species = M_{total}
- Step 3. Absorbed mass = $M_{\text{absorbed}} = M_{\text{total}} - M_{\text{absorbant}}$
- Step 4. % of absorbed species = $(M_{\text{absorbed}}/M_{\text{absorbant}})*100$
- Step 5. 1 mole of absorbed species = MW of absorbed species
- Step 6. Number of moles of absorbed species = $(M_{\text{absorbed}}/\text{MW of absorbed species})$
- Step 7. The number of moles of absorbed species absorbed per gram of absorbant = $(1g/M_{\text{total}})*(\text{Number of moles of absorbed species})$

Solution

- Step 1. $M_{\text{absorbant}} = \text{Mass of PEI-SWNT} = 4.829 \text{ mg}$
- Step 2. $M_{\text{total}} = \text{Mass of PEI-SWNT and CO}_2 = 5.258 \text{ mg}$
- Step 3. $M_{\text{absorbed}} = M_{\text{total}} - M_{\text{absorbant}} = 5.258 \text{ mg} - 4.829 \text{ mg} = 0.429 \text{ mg}$
- Step 4. % of absorbed species = % of CO₂ absorbed = $(M_{\text{absorbed}}/M_{\text{absorbant}})*100 = (0.429/4.829)*100 = 8.8\%$
- Step 5. 1 mole of absorbed species = MW of absorbed species = MW of CO₂ = 44 therefore 1 mole = 44g

- Step 6. Number of moles of absorbed species = ($M_{\text{absorbed}}/\text{MW of absorbed species}$) = (0.429 mg / 44 g) = 9.75 μM
- Step 7. The number of moles of absorbed species absorbed per gram of absorbant = (1 g/ M_{total})*(Number of moles of absorbed species) = (1 g/5.258 mg)*(9.75) = 1.85 mmol of CO_2 absorbed per gram of absorbant

2.5.1.5 Bibliography

- I. W. Chiang, B. E. Brinson, A. Y. Huang, P. A. Willis, M. J. Bronikowski, J. L. Margrave, R. E. Smalley, and R. H. Hauge, *J. Phys. Chem. B*, 2001, **105**, 8297.
- E. P. Dillon, C. A. Crouse and A. R. Barron, *ACS Nano*, 2008, **2**, 156.

2.5.2 TGA/DSC-FTIR Characterization of Oxide Nanaoparticles¹³

2.5.2.1 Metal oxide nanoparticles

The binary compound of one or more oxygen atoms with at least one metal atom that forms a structure ≤ 100 nm is classified as metal oxide (MO_x) nanoparticle. MO_x nanoparticles have exceptional physical and chemical properties (especially if they are smaller than 10 nm) that are strongly related to their dimensions and to their morphology. These enhanced features are due to the increased surface to volume ratio which has a strong impact on the measured binding energies. Based on theoretical models, binding or cohesive energy is inversely related to particle size with a linear relationship (2.39).

$$E_{\text{NP}} = E_{\text{bulk}} \cdot [1 - c \cdot r^{-1}] \quad (2.39)$$

where E_{NP} and E_{bulk} is the binding energy of the nanoparticle and the bulk binding energy respectively, c is a material constant and r is the radius of the cluster. As seen from (2.39), nanoparticles have lower binding energies than bulk material, which means lower electron cloud density and therefore more mobile electrons. This is one of the features that have been identified to contribute to a series of physical and chemical properties.

2.5.2.1.1 Synthesis of metal oxide nanoparticles

Since today, numerous synthetic methods have been developed with the most common ones presented in Table 2.5. These methods have been successfully applied for the synthesis of a variety of materials with 0-D to 3-D complex structures. Among them, the solvothermal methods are by far the most popular ones due to their simplicity. Between the two classes of solvothermal methods, slow decomposition methods, usually called thermal decomposition methods, are preferred over the hot injection methods since they are less complicated, less dangerous and avoid the use of additional solvents.

¹³This content is available online at <<http://cnx.org/content/m23038/1.2/>>.

Method	Characteristics	Advantages	Disadvantages
Solvothermal a) Slow decomposition b) Hot injection	a) Slow heating of M-precursor in the presence of ligand/surfactant precursor b) Injection of M-precursor into solution at high Temp.	a) Safe, easily carried out, variety of M-precursors to use b) Excellent control of particle distribution	a) Poor control of nucleation/growth stages – Particle size b) Hazardous, Reproducibility depends on individual
Template directed	Use of organic molecules or preexistent nanoparticles as templates for directing nanoparticle formation	High yield and high purity of nanoparticles	Template removal in some cases causes particle deformation or loss
Sonochemical	Ultrasound influence particle nucleation	Mild synthesis conditions	Limited applicability
Thermal evaporation	Thermal evaporation of Metal oxides	Monodisperse particle formation, excellent control in shape and structure	Extremely high temperatures, and vacuum system is required
Gas phase catalytic growth	Use of catalyst that serves as a preferential site for absorbing Metal reactants	Excellent control in shape and structure	Limited applicability

Table 2.5: Methods for synthesizing MO_x nanoparticles

A general schematic diagram of the stages involving the nanoparticles formation is shown in Figure 2.38. As seen, first step is the M-atom generation by dissociation of the metal-precursor. Next step is the M-complex formulation, which is carried out before the actual particle assembly stage. Between this step and the final particle formulation, oxidation of the activated complex occurs upon interaction with an oxidant substance. The x-axis is a function of temperature or time or both depending on the synthesis procedure.

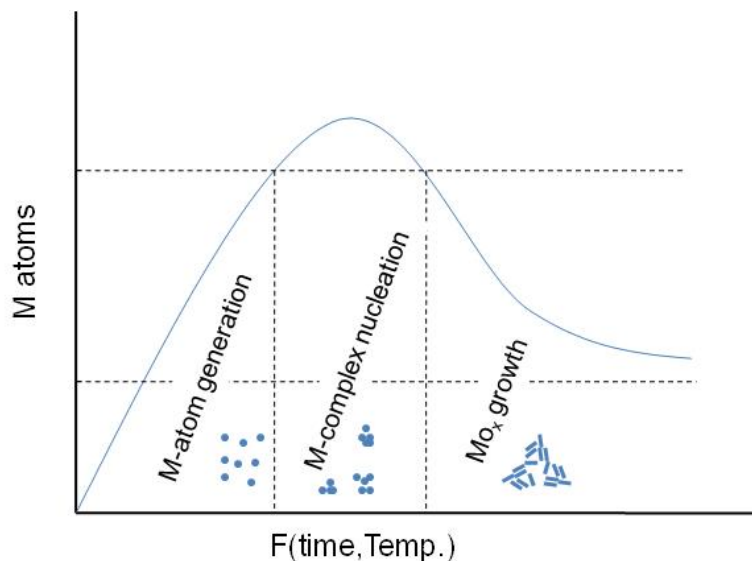


Figure 2.38: Stages of nanoparticle synthesis.

In all cases, the particles synthesized consist of MO_x nanoparticle structures stabilized by one or more types of ligand(s) as seen in Figure 2.39. The ligands are usually long-chained organic molecules that have one more functional groups. These molecules protect the nanoparticles from attracting each other under van der Waals forces and therefore prevent them from aggregating.

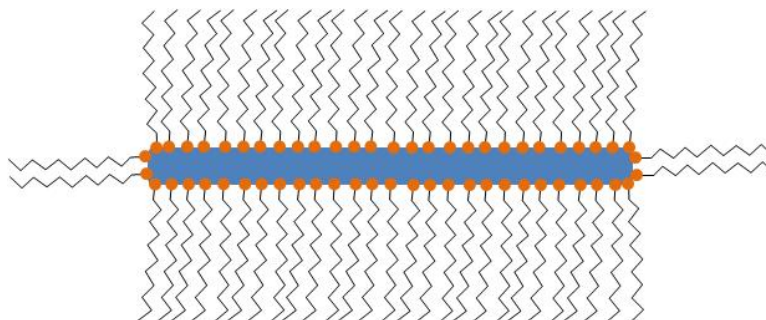


Figure 2.39: Schematic representation of a surfactant/ligand stabilized nanoparticle.

Even though often not referred to specifically, all particles synthesized are stabilized by organic (hydrophilic, hydrophobic or amphoteric) ligands. The detection and the understanding of the structure of these ligands can be of critical importance for understanding the controlling the properties of the synthesized nanoparticles.

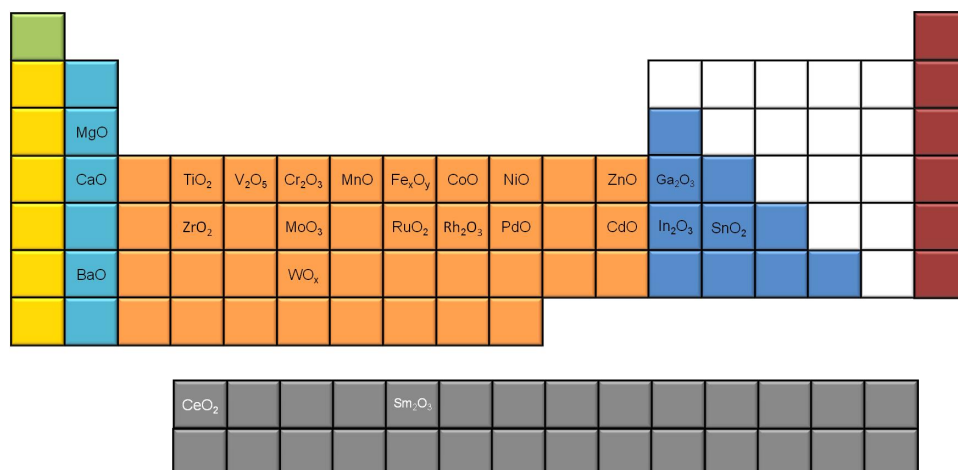
2.5.2.1.1.1 Metal oxide nanoparticles synthesized via slow decomposition

In this work, we refer to MO_x nanoparticles synthesized via slow decomposition of a metal complex. In Table 2.6, a number of different MO_x nanoparticles are presented, synthesized via metal complex dissociation. Metal- MO_x and mixed MO_x nanoparticles are not discussed here.

Metal oxide	Shape	Size (approx.)
Cerium oxide	dots	5-20 nm
Iron oxide	dots, cubes	8.5-23.4 nm
Manganese oxide	Multipods	>50 nm
Zinc oxide	Hexagonal pyramid	15-25 nm
Cobalt oxide	dots	~ 10 nm
Chromium oxide	dots	12 nm
Vanadium oxide	dots	9-15 nm
Molybdenum oxide	dots	5 nm
Rhodium oxide	dots, rods	16 nm
Palladium oxide	dots	18 nm
Ruthenium oxide	dots	9-14 nm
Zirconium oxide	rods	7x30 nm
Barium oxide	dots	20 nm
Magnesium oxide	dots	4-8 nm
Calcium oxide	dots, rods	7-12 nm
Nickel oxide	dots	8-15 nm
Titanium oxide	dots and rods	2.3-30 nm
Tin oxide	dots	2.0-5.0 nm
Indium oxide	dots	~ 5 nm
Samaria	Square	~ 10 nm

Table 2.6: Examples of MO_x nanoparticles synthesized via decomposition of metal complexes.

A significant number of metal oxides synthesized using slow decomposition is reported in literature. If we use the periodic table to map the different MO_x nanoparticles (Figure 2.40), we notice that most of the alkali and transition metals generate MO_x nanoparticles, while only a few of the poor metals seem to do so, using this synthetic route. Moreover, two of the rare earth metals (Ce and Sm) have been reported to successfully give metal oxide nanoparticles via slow decomposition.



Among the different characterization techniques used for defining these structures, transition electron microscopy (TEM) holds the lion's share. Nevertheless, most of the modern characterization methods are more important when it comes to understanding the properties of nanoparticles. X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), nuclear magnetic resonance (NMR), IR spectroscopy, Raman spectroscopy, and thermogravimetric analysis (TGA) methods are systematically used for characterization.

2.5.2.1.2 Synthesis and characterization of WO_{3-x} nanorods

The synthesis of WO_{3-x} nanorods is based on the method published by Lee et al. A slurry mixture of Me₃NO•2H₂O, oleylamine and W(CO)₆ was heated up to 250 °C at a rate of 3 °C/min (Figure 2.41). The mixture was aged at this temperature for 3 hours before cooling down to room temperature.

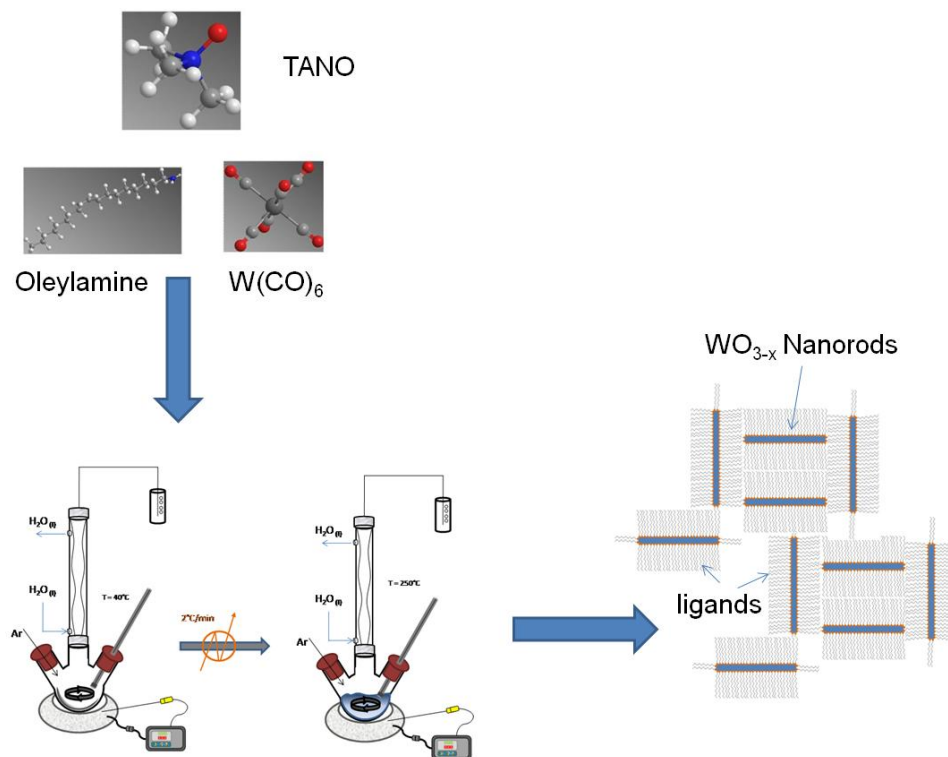


Figure 2.41: Experimental setup for synthesis of WO_{3-x} nanorods.

Multiple color variations were observed between 100 - 250 °C with the final product having a dark blue color. Tungsten oxide nanorods ($W_{18}O_{49}$ identified by XRD) with a diameter of 7 ± 2 nm and 50 ± 2 nm long were acquired after centrifugation of the product solution. A TEM image of the $W_{18}O_{49}$ nanorods is shown in Figure 2.42.

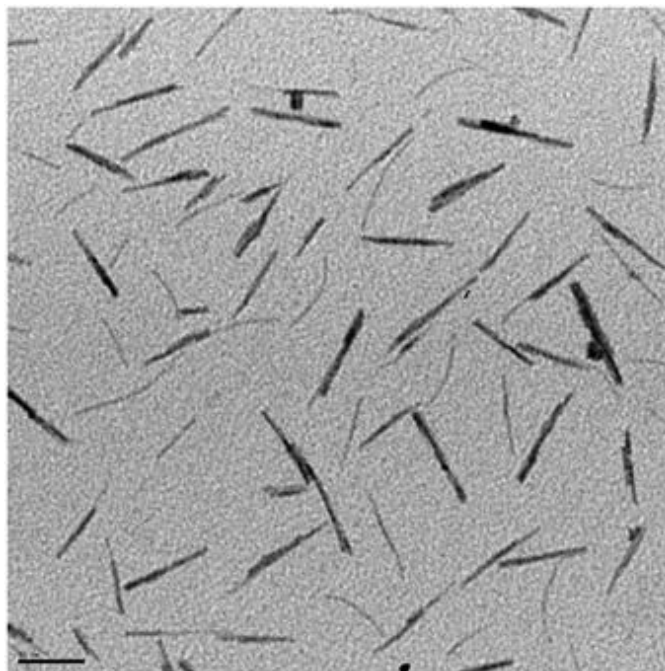


Figure 2.42: TEM image of WO_{3-x} nanorods.

2.5.2.2 Thermogravimetric analysis (TGA)/differential scanning calorimetry (DSC)

Thermogravimetric analysis (TGA) is a technique widely used for determining the organic and inorganic content of various materials. Its basic rule of function is the high precision measurement of weight gain/loss with increasing temperature under inert or reactive atmospheres. Each weight change corresponds to physical (crystallization, phase transformation) or chemical (oxidation, reduction, reaction) processes that take place by increasing the temperature. The sample is placed into platinum or alumina pan and along with an empty or standard pan are placed onto two high precision balances inside a high temperature oven. A method for pretreating the samples is selected and the procedure is initiated. Differential scanning calorimetry (DSC) is a technique usually accompanying TGA and is used for calculating enthalpy energy changes or heat capacity changes associated with phase transitions and/or ligand-binding energy cleavage.

In Figure 2.43 the TGA/DSC plot acquired for the ligand decomposition of WO_{3-x} nanorods is presented. The sample was heated at constant rate under N_2 atmosphere up to 195 °C for removing moisture and then up to 700 °C for removing the oleylamine ligands. It is important to use an inert gas for performing such a study to avoid any premature oxidation and/or capping agent combustion. 26.5% of the weight loss is due to oleylamine evaporations which means about 0.004 moles per gram of sample. After isothermal heating at 700 °C for 25 min the flow was switched to air for oxidizing the ligand-free WO_{3-x} to WO_3 . From the DSC curve we noticed the following changes of the weight corrected heat flow:

1. From 0 – 10 min assigned to water evaporation.
2. From 65 – 75 min assigned to OA evaporation.
3. From 155 – 164 min assigned to WO_{3-x} oxidation.
4. From 168 – 175 min is also due to further oxidation of W^{5+} atoms.

The heat flow increase during the WO_{3-x} to WO_3 oxidation is proportional to the crystal phase defects (or W atoms of oxidation state +5) and can be used for performing qualitative studies between different WO_x nanoparticles.

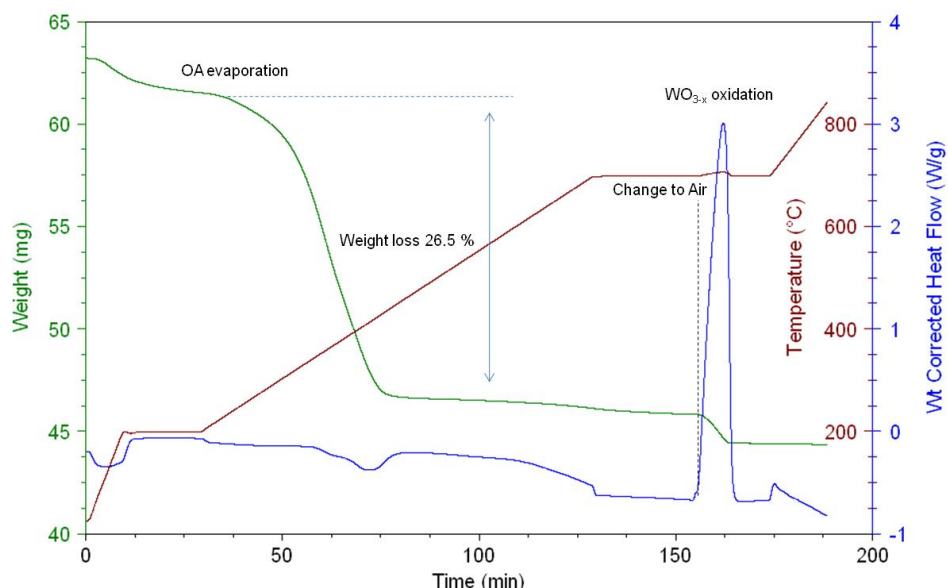


Figure 2.43: TGA/DSC plot for WO_{3-x} nanorods.

The detailed information about the procedure used to acquire the TGA/DSC plot shown in Figure 2.43 is as follows.

- Step 1. Select gas (N_2 with flow rate 50 mL/min.)
- Step 2. Ramp 20 $^{\circ}\text{C}/\text{min}$ to 200 $^{\circ}\text{C}$.
- Step 3. Isothermal for 20 min.
- Step 4. Ramp 5 $^{\circ}\text{C}/\text{min}$ to 700 $^{\circ}\text{C}$.
- Step 5. Isothermal for 25 min.
- Step 6. Select gas (air).
- Step 7. Isothermal for 20 min.
- Step 8. Ramp 10 $^{\circ}\text{C}/\text{min}$ to 850 $^{\circ}\text{C}$.
- Step 9. Cool down

2.5.2.3 Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) is the most popular spectroscopic method used for characterizing organic and inorganic compounds. The basic modification of an FTIR from a regular IR instrument is a device called interferometer, which generates a signal that allows very fast IR spectrum acquisition. For doing so, the generated interferogram has to be “expanded” using a Fourier transformation to generate a

complete IR frequency spectrum. In the case of performing FTIR transmission studies the intensity of the transmitted signal is measured and the IR fingerprint is generated (2.40).

$$T = \frac{I}{I_b} = e^{c\epsilon l} \quad (2.40)$$

Where I is the intensity of the samples, I_b is the intensity of the background, c is the concentration of the compound, ϵ is the molar extinction coefficient and l is the distance that light travels through the material. A transformation of transmission to absorption spectra is usually performed and the actual concentration of the component can be calculated by applying the Beer-Lambert law (2.41).

$$A = -\ln(T) = c\epsilon l \quad (2.41)$$

A qualitative IR-band map is presented in Figure 2.44. The absorption bands between 4000 to 1600 cm^{-1} represent the group frequency region and are used to identify the stretching vibrations of different bonds. At lower frequencies (from 1600 to 400 cm^{-1}) vibrations due to intermolecular bond bending occurs upon IR excitation and therefore are usually not taken into account.

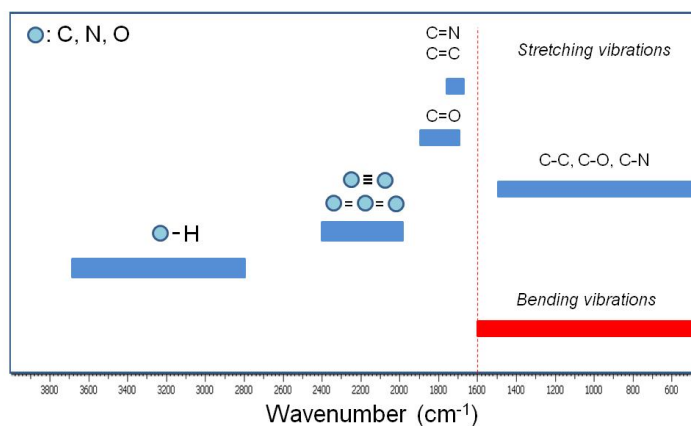


Figure 2.44: Selected FTIR stretching and bending modes associated with the typical ligands used for nanoparticle stabilization.

2.5.2.4 TGA/DSC-FTIR characterization

TGA/DSC is a powerful tool for identifying the different compounds evolved during the controlled pyrolysis and therefore provide qualitative and quantitative information about the volatile components of the sample. In metal oxide nanoparticle synthesis TGA/DSC-FTIR studies can provide qualitative and quantitative information about the volatile compounds of the nanoparticles.

TGA-FTIR results presented below were acquired using a Q600 Simultaneous TGA/DSC (SDT) instrument online with a Nicolet 5700 FTIR spectrometer. This system has a digital mass flow control and two gas inlets giving the capability to switch reacting gas during each run. It allows simultaneous weight change and differential heat flow measurements up to 1500 °C, while at the same time the outflow line is connected to the FTIR for performing gas phase compound identification. Grand-Schmidt thermographs were usually constructed to present the species evolution with time in 3 dimensions.

Selected IR spectra are presented in Figure 2.45. Four regions with intense peaks are observed. Between $4000 - 3550\text{ cm}^{-1}$ due to O-H bond stretching assigned to H_2O that is always present and due to N-H group stretching that is assigned to the amine group of oleylamine. Between $2400 - 2250\text{ cm}^{-1}$ due to $\text{O}=\text{C}=\text{O}$ stretching, between $1900 - 1400\text{ cm}^{-1}$ which is mainly to C=O stretching and between $800 - 400\text{ cm}^{-1}$ cannot be resolved as explained previously.

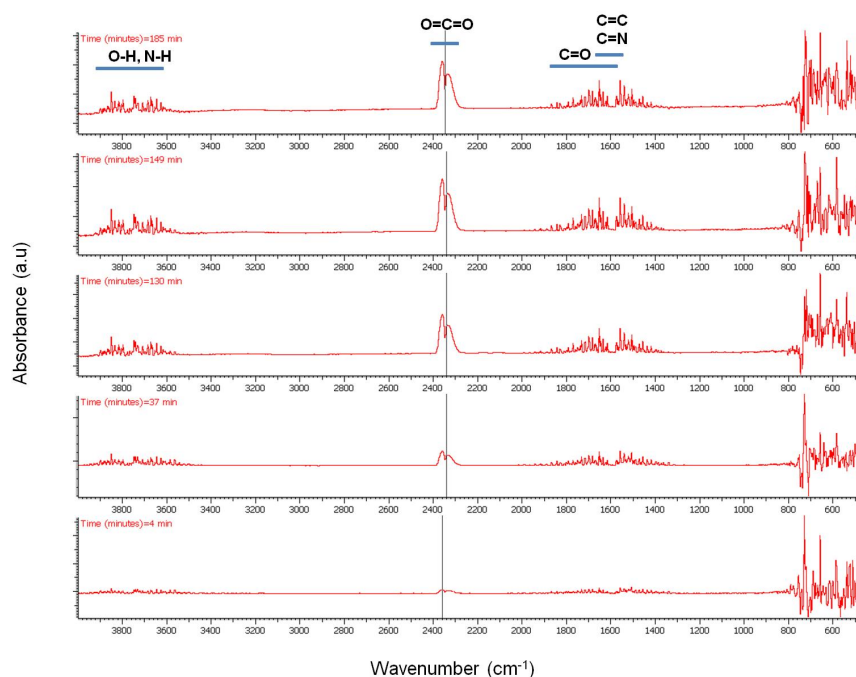


Figure 2.45: FTIR spectra of products from WO_{3-x} pyrolysis.

The peak intensity evolution with time can be more easily observed in Figure 2.46 and Figure 2.47. As seen, CO_2 evolution increases significantly with time especially after switching our flow from N_2 to air. H_2O seems to be present in the outflow stream up to 700°C while the majority of the N-H amine peaks seem to disappear at about 75 min. C=N compounds are not expected to be present in the stream which leaves bands between $1900 - 1400\text{ cm}^{-1}$ assigned to C=C and C=O stretching vibrations. Unsaturated olefins resulting from the cracking of the oleylamine molecule are possible at elevated temperatures as well as the presence of CO especially under N_2 atmosphere.

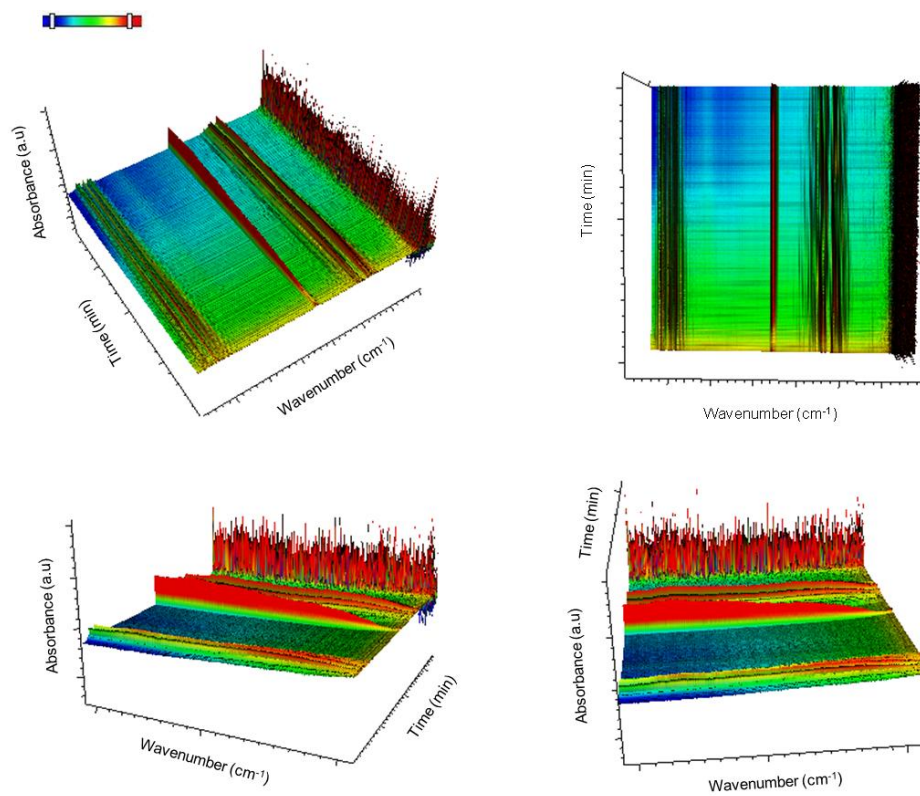


Figure 2.46: 3D representation of FTIR Spectra of the volatile compounds of WO_{3-x} .

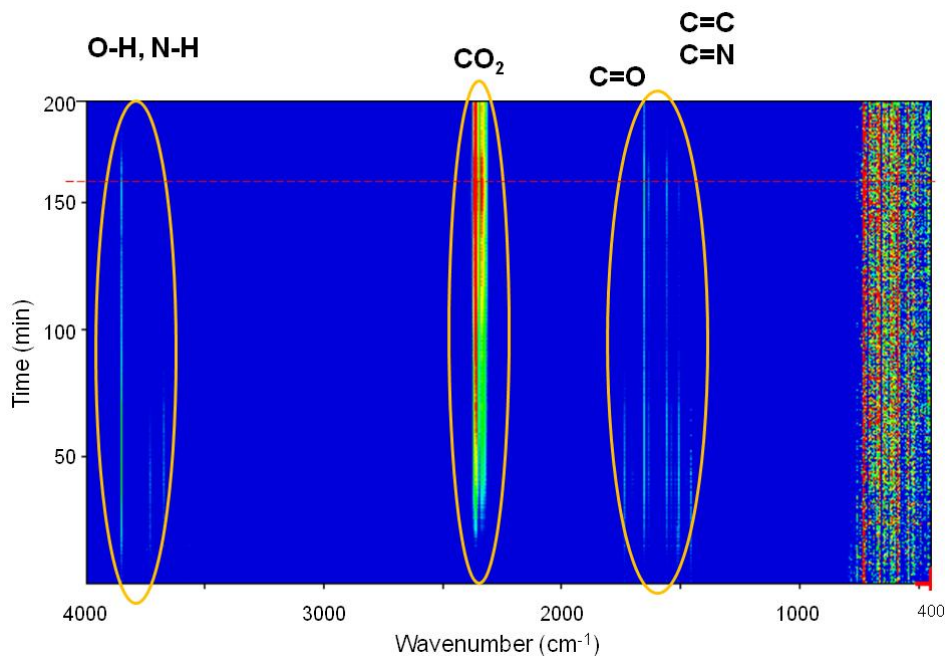


Figure 2.47: Intensity profile of FTIR spectra of the volatile compounds formed from the pyrolysis of WO_{3-x} .

From the above compound identification we can summarize and propose the following applications for TGA-FTIR. First, more complex ligands, containing aromatic rings and maybe other functional groups may provide more insight in the ligand to MO_x interaction. Second, the presence of CO and CO_2 even under N_2 flow means that complete O_2 removal from the TGA and the FTIR cannot be achieved under these conditions. Even though the system was equilibrated for more than an hour, traces of O_2 are existent which create errors in our calculations.

2.5.2.5 Bibliography

- R. D. Parra and H. H. Farrell, *J. Phys. Chem. C*, 2009, **113**, 4786.
- S. C. Vanithakumari and K. K. Nanda, *J. Phys. Chem. B*, 2006, **110**, 6985.
- M. Wautelet and D. Duivivier, *Eur. J. Phys.*, 2007, **28**, 953.
- X. Wang and Y. Li, *J. Am. Chem. Soc.*, 2002, **124**, 2880.
- F. K. R. N. Greta and R. Patzke, *Angew. Chem., Int. Ed.*, 2002, **41**, 2446.
- Z. W. Pan, Z. R. Dai, and Z. L. Wang, *Science*, 2001, **291**, 1947.
- H. Gu and M. D. Soucek, *Chem. Mater.*, 2007, **19**, 1103.
- L. M. Bronstein, X. Huang, J. Retrum, A. Schmucker, M. Pink, B. D. Stein, and B. Dragnea, *Chem. Mater.*, 2007, **19**, 3624.
- D. Zitoun, N. Pinna, N. Frolet, and C. Belin, *J. Am. Chem. Soc.*, 2005, **127**, 15034.
- S. -H. Choi, E. -G. Kim, J. Park, K. An, N. Lee, S. C. Kim, and T. Hyeon, *J. Phys. Chem., B*, 2005, **109**, 14792.
- M. Epifani, J. Arbiol, R. Diaz, M. J. Peralvarez, P. Siciliano, and J. R. Morante, *Chem. Mater.*, 2005, **17**, 6468.

- T. Yu, J. Joo, Y. I. Park, and T. Hyeon, *J. Am. Chem. Soc.*, 2006, **128**, 1786.
- K. Lee, W. S. Seo, and J. T. Park, *J. Am. Chem. Soc.*, 2003, **125**, 3408.
- C. A. Emeis, *J. Catalysis*, 1993, **141**, 347.
- P. R. Griffiths, J. A. De Haseth, *Fourier Transform Infrared Spectrometry*. Wiley-Interscience, New York (2007)

2.5.3 Determination of Sublimation Enthalpy and Vapor Pressure for Inorganic and Metal-Organic Compounds by Thermogravimetric Analysis¹⁴

2.5.3.1 Introduction

Metal compounds and complexes are invaluable precursors for the chemical vapor deposition (CVD) of metal and non-metal thin films. In general, the precursor compounds are chosen on the basis of their relative volatility and their ability to decompose to the desired material under a suitable temperature regime. Unfortunately, many readily obtainable (commercially available) compounds are not of sufficient volatility to make them suitable for CVD applications. Thus, a *prediction* of the volatility of a metal-organic compounds as a function of its ligand identity and molecular structure would be desirable in order to determine the suitability of such compounds as CVD precursors. Equally important would be a method to determine the vapor pressure of a potential CVD precursor as well as its optimum temperature of sublimation.

It has been observed that for organic compounds it was determined that a rough proportionality exists between a compound's melting point and sublimation enthalpy; however, significant deviation is observed for inorganic compounds.

Enthalpies of sublimation for metal-organic compounds have been previously determined through a variety of methods, most commonly from vapor pressure measurements using complex experimental systems such as Knudsen effusion, temperature drop microcalorimetry and, more recently, differential scanning calorimetry (DSC). However, the measured values are highly dependent on the experimental procedure utilized. For example, the reported sublimation enthalpy of $\text{Al}(\text{acac})_3$ (Figure 2.48a, where $\text{M} = \text{Al}$, $n = 3$) varies from 47.3 to 126 kJ/mol.

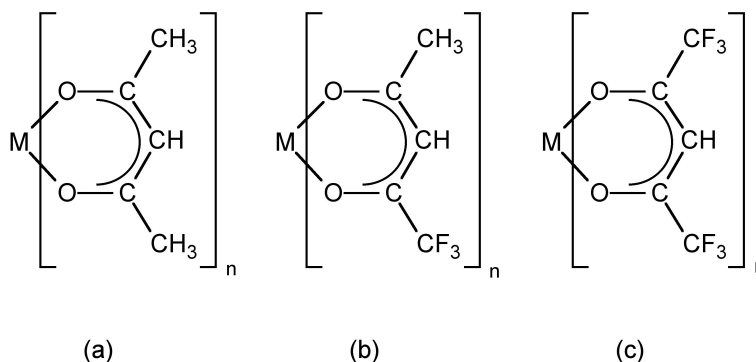


Figure 2.48: Structure of a typical metal β -diketonate complex. (a) acetylacetonate (acac); (b) trifluoroacetylacetonate (tfac), and (c) hexafluoroacetylacetonate (hfac).

Thermogravimetric analysis offers a simple and reproducible method for the determination of the vapor pressure of a potential CVD precursor as well as its enthalpy of sublimation.

¹⁴This content is available online at <<http://cnx.org/content/m33649/1.2/>>.

2.5.3.2 Determination of sublimation enthalpy

The enthalpy of sublimation is a quantitative measure of the volatility of a particular solid. This information is useful when considering the feasibility of a particular precursor for CVD applications. An ideal sublimation process involves no compound decomposition and only results in a solid-gas phase change, i.e., (2.42).



Since phase changes are thermodynamic processes following zero-order kinetics, the evaporation rate or rate of mass loss by sublimation (m_{sub}), at a constant temperature (T), is constant at a given temperature, (2.43). Therefore, the m_{sub} values may be directly determined from the linear mass loss of the TGA data in isothermal regions.

$$m_{\text{sub}} = \frac{\Delta[\text{mass}]}{\Delta t} \quad (2.43)$$

The thermogravimetric and differential thermal analysis of the compound under study is performed to determine the temperature of sublimation and thermal events such as melting. Figure 2.49 shows a typical TG/DTA plot for a gallium chalcogenide cubane compound (Figure 2.50).

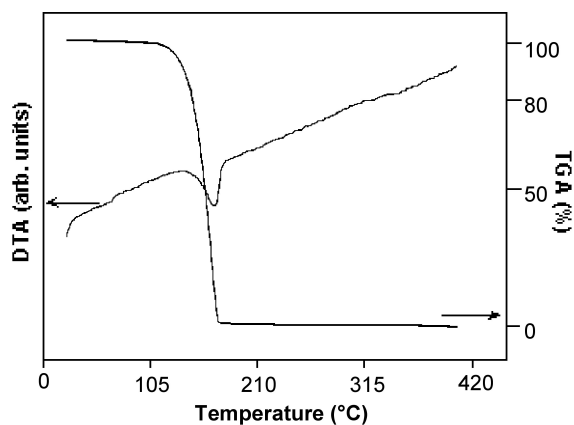


Figure 2.49: A typical thermogravimetric/differential thermal analysis (TG/DTA) analysis of $[(\text{EtMe}_2\text{C})\text{GaSe}]_4$, whose structure is shown in Figure 2.50. Adapted from E. G. Gillan, S. G. Bott, and A. R. Barron, *Chem. Mater.*, 1997, **9**, 3, 796.

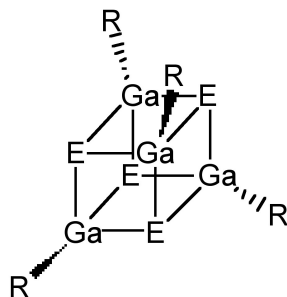


Figure 2.50: Structure of gallium chalcogenide cubane compound, where E = S, Se, and R = CMe₃, CMe₂Et, CEt₂Me, CEt₃.

2.5.3.2.1 Data collection

In a typical experiment 5 - 10 mg of sample is used with a heating rate of ca. 5 °C/min up to under either a 200-300 mL/min inert (N₂ or Ar) gas flow or a dynamic vacuum (ca. 0.2 Torr if using a typical vacuum pump). The argon flow rate was set to 90.0 mL/min and was carefully monitored to ensure a steady flow rate during runs and an identical flow rate from one set of data to the next.

Once the temperature range is defined, the TGA is run with a preprogrammed temperature profile (Figure 2.51). It has been found that sufficient data can be obtained if each isothermal mass loss is monitored over a period (between 7 and 10 minutes is found to be sufficient) before moving to the next temperature plateau. In all cases it is important to confirm that the mass loss at a given temperature is linear. If it is not, this can be due to either (a) temperature stabilization had not occurred and so longer times should be spent at each isotherm, or (b) decomposition is occurring along with sublimation, and lower temperature ranges must be used. The slope of each mass drop is measured and used to calculate sublimation enthalpies as discussed below.

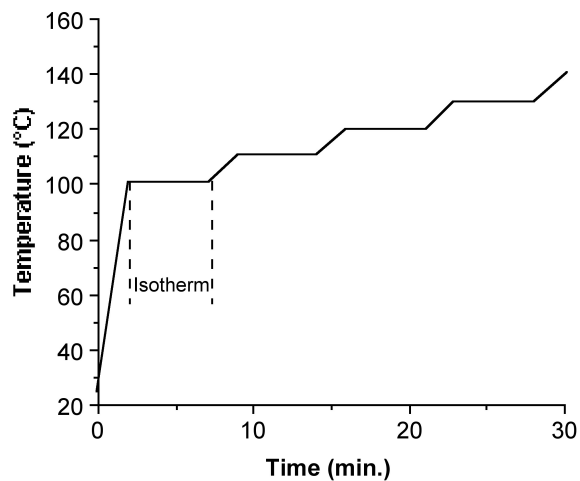


Figure 2.51: A typical temperature profile for determination of isothermal mass loss rate.

As an illustrative example, Figure 2.52 displays the data for the mass loss of $\text{Cr}(\text{acac})_3$ (Figure 2.48a, where $M = \text{Cr}$, $n = 3$) at three isothermal regions under a constant argon flow. Each isothermal data set should exhibit a linear relation. As expected for an endothermal phase change, the linear slope, equal to m_{sub} , increases with increasing temperature.

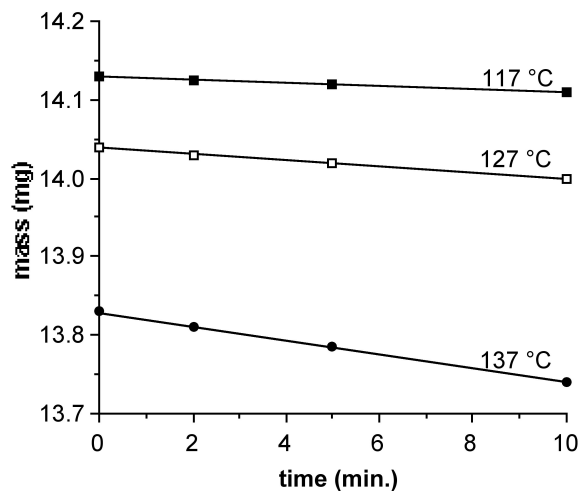


Figure 2.52: Plot of TGA results for $\text{Cr}(\text{acac})_3$ performed at different isothermal regions. Adapted from B. D. Fahlman and A. R. Barron, *Adv. Mater. Optics Electron.*, 2000, **10**, 223.

NOTE: Samples of iron acetylacetonate (Figure 2.48a, where $M = \text{Fe}$, $n = 3$) may be used as a calibration standard through ΔH_{sub} determinations before each day of use. If the measured value of the sublimation enthalpy for $\text{Fe}(\text{acac})_3$ is found to differ from the literature value by more than 5%, the sample is re-analyzed and the flow rates are optimized until an appropriate value is obtained. Only after such a calibration is optimized should other complexes be analyzed. It is important to note that while small amounts ($< 10\%$) of involatile impurities will not interfere with the ΔH_{sub} analysis, competitively volatile impurities will produce higher apparent sublimation rates.

It is important to discuss at this point the various factors that must be controlled in order to obtain meaningful (useful) m_{sub} data from TGA data.

1. The sublimation rate is independent of the amount of material used but may exhibit some dependence on the flow rate of an inert carrier gas, since this will affect the equilibrium concentration of the cubane in the vapor phase. While little variation was observed we decided that for consistency m_{sub} values should be derived from vacuum experiments only.
2. The surface area of the solid in a given experiment should remain approximately constant; otherwise the sublimation rate (i.e., mass/time) at different temperatures cannot be compared, since as the relative surface area of a given crystallite decreases during the experiment the apparent sublimation rate will also decrease. To minimize this problem, data was taken over a small temperature ranges (ca. 30°C), and overall sublimation was kept low (ca. 25% mass loss representing a surface area change of less than 15%). In experiments where significant surface area changes occurred the values of m_{sub} deviated significantly from linearity on a $\log(m_{\text{sub}})$ versus $1/T$ plot.
3. The compound being analyzed must not decompose to any significant degree, because the mass changes due to decomposition will cause a reduction in the apparent m_{sub} value, producing erroneous results. With a simultaneous TG/DTA system it is possible to observe exothermic events if decomposition occurs, however the clearest indication is shown by the mass loss versus time curves which are no longer linear but exhibit exponential decays characteristic of first or second order decomposition processes.

2.5.3.2.2 Data analysis

The basis of analyzing isothermal TGA data involves using the Clausius-Clapeyron relation between vapor pressure (p) and temperature (T), (2.44), where ΔH_{sub} is the enthalpy of sublimation and R is the gas constant (8.314 J/K.mol).

$$\frac{d \ln(p)}{dT} = \frac{\Delta H_{\text{sub}}}{RT^2} \quad (2.44)$$

Since m_{sub} data are obtained from TGA data, it is necessary to utilize the Langmuir equation, (2.45), that relates the vapor pressure of a solid with its sublimation rate.

$$p = \left[\frac{2\pi RT}{M_w} \right]^{0.5} m_{\text{sub}} \quad (2.45)$$

After integrating (2.44) in log form, substituting in (2.45), and consolidating the constants, one obtains the useful equality, (2.46).

$$\log(m_{\text{sub}}\sqrt{T}) = \frac{-0.0522(\Delta H_{\text{sub}})}{T} + \left[\frac{0.0522(\Delta H_{\text{sub}})}{T_{\text{sub}}} - \frac{1}{2} \log\left(\frac{1306}{M_w}\right) \right] \quad (2.46)$$

Hence, the linear slope of a $\log(m_{\text{sub}}T^{1/2})$ versus $1/T$ plot yields ΔH_{sub} . An example of a typical plot and the corresponding ΔH_{sub} value is shown in Figure 2.53. In addition, the y intercept of such a plot provides a value for T_{sub} , the calculated sublimation temperature at atmospheric pressure.

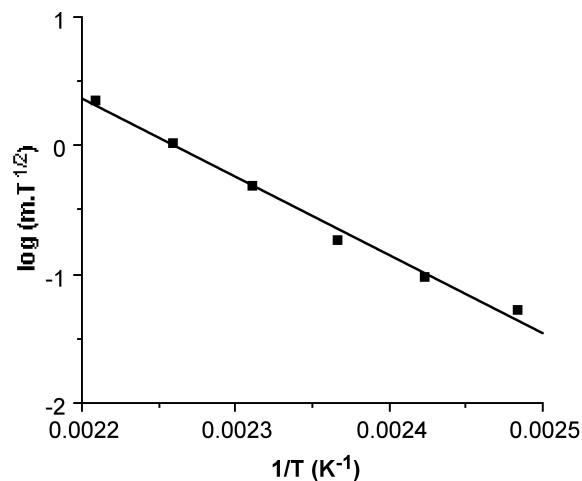


Figure 2.53: Plot of $\log(m_{\text{sub}} T^{1/2})$ versus $1/T$ and the determination of the ΔH_{sub} (112.6 kJ/mol) for $\text{Fe}(\text{acac})_3$ ($R^2 = 0.9989$). Adapted from B. D. Fahlman and A. R. Barron, *Adv. Mater. Optics Electron.*, 2000, **10**, 223.

Table 2.7 lists the typical results using the TGA method for a variety of metal β -diketonates, while Table 2.8 lists similar values obtained for gallium chalcogenide cubane compounds.

Compound	ΔH_{sub} (kJ/mol)	ΔS_{sub} (J/K.mol)	$T_{\text{sub calc.}}$ ($^{\circ}\text{C}$)	Calculated vapor pressure @ 150°C (Torr)
$\text{Al}(\text{acac})_3$	93	220	150	3.261
$\text{Al}(\text{tfac})_3$	74	192	111	9.715
$\text{Al}(\text{hfac})_3$	52	152	70	29.120
$\text{Cr}(\text{acac})_3$	91	216	148	3.328
$\text{Cr}(\text{tfac})_3$	71	186	109	9.910
$\text{Cr}(\text{hfac})_3$	46	134	69	29.511
$\text{Fe}(\text{acac})_3$	112	259	161	2.781
$\text{Fe}(\text{tfac})_3$	96	243	121	8.340
continued on next page				

Fe(hfac) ₃	60	169	81	25.021
Co(acac) ₃	138	311	170	1.059
Co(tfac) ₃	119	295	131	3.319
Co(hfac) ₃	73	200	90	9.132

Table 2.7: Selected thermodynamic data for metal β -diketonate compounds determined from thermogravimetric analysis. Data from B. D. Fahlman and A. R. Barron, *Adv. Mater. Optics Electron.*, 2000, **10**, 223.

Compound	ΔH_{sub} (kJ/mol)	ΔS_{sub} (J/K.mol)	T_{sub} calc. ($^{\circ}\text{C}$)	Calculated vapor pressure @ 150 $^{\circ}\text{C}$ (Torr)
[(Me ₃ C)GaS] ₄	110	300	94	22.75
[(EtMe ₂ C)GaS] ₄	124	330	102	18.89
[(Et ₂ MeC)GaS] ₄	137	339	131	1.173
[(Et ₃ C)GaS] ₄	149	333	175	0.018
[(Me ₃ C)GaSe] ₄	119	305	116	3.668
[(EtMe ₂ C)GaSe] ₄	137	344	124	2.562
[(Et ₂ MeC)GaSe] ₄	147	359	136	0.815
[(Et ₃ C)GaSe] ₄	156	339	189	0.005

Table 2.8: Selected thermodynamic data for gallium chalcogenide cubane compounds determined from thermogravimetric analysis. Data from E. G. Gillan, S. G. Bott, and A. R. Barron, *Chem. Mater.*, 1997, **9**, 3, 796.

A common method used to enhance precursor volatility and corresponding efficacy for CVD applications is to incorporate partially (Figure 2.48b) or fully (Figure 2.48c) fluorinated ligands. As may be seen from Table 2.7 this substitution does results in significant decrease in the ΔH_{sub} , and thus increased volatility. The observed enhancement in volatility may be rationalized either by an increased amount of intermolecular repulsion due to the additional lone pairs or that the reduced polarizability of fluorine (relative to hydrogen) causes fluorinated ligands to have less intermolecular attractive interactions.

2.5.3.3 Determination of sublimation entropy

The entropy of sublimation is readily calculated from the ΔH_{sub} and the calculated T_{sub} data, (2.47).

$$\Delta S_{\text{sub}} = \frac{\Delta H_{\text{sub}}}{T_{\text{sub}}} \quad (2.47)$$

Table 2.7 and Table 2.8 show typical values for metal β -diketonate compounds and gallium chalcogenide cubane compounds, respectively. The range observed for gallium chalcogenide cubane compounds ($\Delta S_{\text{sub}} = 330 \pm 20$ J/K.mol) is slightly larger than values reported for the metal β -diketonates compounds ($\Delta S_{\text{sub}} = 130 - 330$ J/K.mol) and organic compounds (100 - 200 J/K.mol), as would be expected for a transformation giving translational and internal degrees of freedom. For any particular chalcogenide, i.e., [(R)GaS]₄, the lowest ΔS_{sub} are observed for the Me₃C derivatives, and the largest ΔS_{sub} for the Et₂MeC derivatives, see Table 2.8. This is in line with the relative increase in the modes of freedom for the alkyl groups in the absence of crystal packing forces.

2.5.3.4 Determination of vapor pressure

While the sublimation temperature is an important parameter to determine the suitability of a potential precursor compounds for CVD, it is often preferable to express a compound's volatility in terms of its vapor pressure. However, while it is relatively straightforward to determine the vapor pressure of a liquid or gas, measurements of solids are difficult (e.g., use of the isoteniscopic method) and few laboratories are equipped to perform such experiments. Given that TGA apparatus are increasingly accessible, it would therefore be desirable to have a simple method for vapor pressure determination that can be accomplished on a TGA.

Substitution of (2.43) into (2.45) allows for the calculation of the vapor pressure (p) as a function of temperature (T). For example, Figure 2.54 shows the calculated temperature dependence of the vapor pressure for $[(\text{Me}_3\text{C})\text{GaS}]_4$. The calculated vapor pressures at 150 °C for metal β -diketonates compounds and gallium chalcogenide cubane compounds are given in Table 2.7 and Table 2.8.

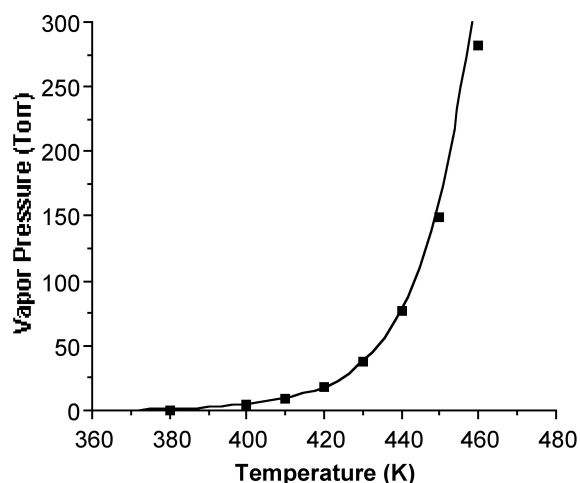


Figure 2.54: A plot of calculated vapor pressure (Torr) against temperature (K) for $[(\text{Me}_3\text{C})\text{GaS}]_4$. Adapted from E. G. Gillan, S. G. Bott, and A. R. Barron, *Chem. Mater.*, 1997, **9**, 3, 796.

The TGA approach to show reasonable agreement with previous measurements. For example, while the value calculated for $\text{Fe}(\text{acac})_3$ (2.78 Torr @ 113 °C) is slightly higher than that measured directly by the isoteniscopic method (0.53 Torr @ 113 °C); however, it should be noted that measurements using the sublimation bulb method obtained values much lower (8×10^{-3} Torr @ 113 °C). The TGA method offers a suitable alternative to conventional (direct) measurements of vapor pressure.

2.5.3.5 Bibliography

- P. W. Atkins, *Physical Chemistry*, 5th ed., W. H. Freeman, New York (1994).
- G. Beech and R. M. Lintonbon, *Thermochim. Acta*, 1971, **3**, 97.
- B. D. Fahlman and A. R. Barron, *Adv. Mater. Optics Electron.*, 2000, **10**, 223.
- E. G. Gillan, S. G. Bott, and A. R. Barron, *Chem. Mater.*, 1997, **9**, 3, 796.
- J. O. Hill and J. P. Murray, *Rev. Inorg. Chem.*, 1993, **13**, 125.
- J. P. Murray, K. J. Cavell and J. O. Hill, *Thermochim. Acta*, 1980, **36**, 97.
- M. A. V. Ribeiro da Silva and M. L. C. C. H. Ferrao, *J. Chem. Thermodyn.*, 1994, **26**, 315.
- R. Sabbah, D. Tabet, S. Belaadi, *Thermochim. Acta*, 1994, **247**, 193.

- L. A. Torres-Gomez, G. Barreiro-Rodriguez, and A. Galarza-Mondragon, *Thermochim. Acta*, 1988, **124**, 229.

2.6 Differential Scanning Calorimetry (DSC) ¹⁵

2.6.1 Introduction

Differential scanning calorimetry (DSC) is a technique used to measure the difference in the heat flow rate of a sample and a reference over a controlled temperature range. These measurements are used to create phase diagrams and gather thermoanalytical information such as transition temperatures and enthalpies.

2.6.1.1 History

DSC was developed in 1962 by Perkin-Elmer employees Emmett Watson and Michael O'Neill and was introduced at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy (Figure 2.55). The equipment for this technique was available to purchase beginning in 1963 and has evolved to control temperatures more accurately and take measurements more precisely, ensuring repeatability and high sensitivity.

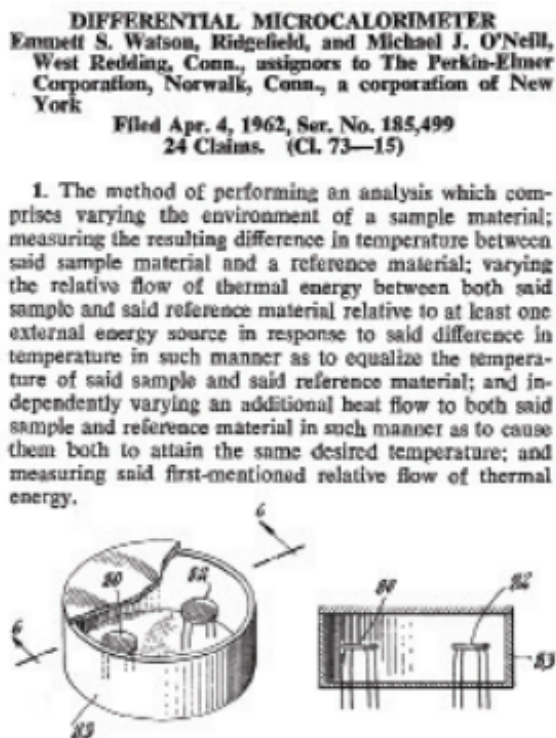


Figure 2.55: An excerpt from the original DSC patent.

¹⁵This content is available online at <<http://cnx.org/content/m43548/1.1/>>.

2.6.2 Theory

2.6.2.1 Phase transitions

Phase transitions refer to the transformation from one state of matter to another. Solids, liquids, and gasses are changed to other states as the thermodynamic system is altered, thereby affecting the sample and its properties. Measuring these transitions and determining the properties of the sample is important in many industrial settings and can be used to ensure purity and determine composition (such as with polymer ratios). Phase diagrams (Figure 2.56) can be used to clearly demonstrate the transitions in graphical form, helping visualize the transition points and different states as the thermodynamic system is changed.

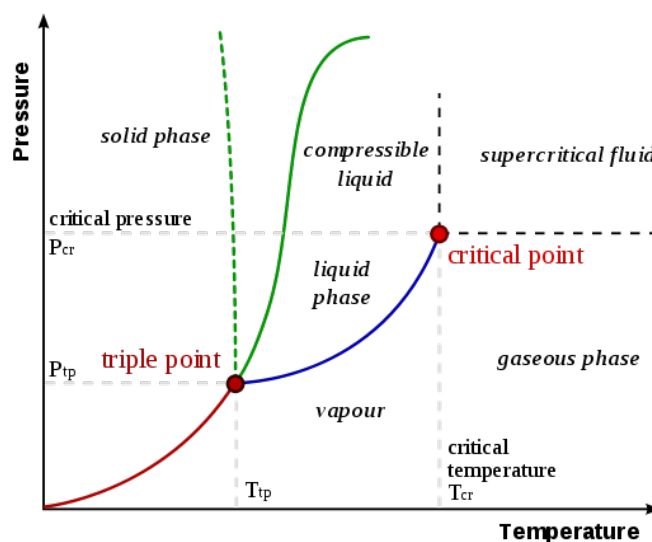


Figure 2.56: An example of a typical phase diagram.

2.6.2.2 Differential thermal analysis

Prior to DSC, differential thermal analysis (DTA) was used to gather information about transition states of materials. In DTA, the sample and reference are heated simultaneously with the same amount of heat and the temperature of each is monitored independently. The difference between the sample temperature and the reference temperature gives information about the exothermic or endothermic transition occurring in the sample. This strategy was used as the foundation for DSC, which sought to measure the difference in energy needed to keep the temperatures the same instead of measure the difference in temperature from the same amount of energy.

2.6.2.3 Differential scanning calorimeter

Instead of measuring temperature changes as heat is applied as in DTA, DSC measures the amount of heat that is needed to increase the temperatures of the sample and reference across a temperature gradient. The sample and reference are kept at the same temperature as it changes across the gradient, and the differing amounts of heat required to keep the temperatures synchronized are measured. As the sample undergoes

phase transitions, more or less heat is needed, which allows for phase diagrams to be created from the data. Additionally, specific heat, glass transition temperature, crystallization temperature, melting temperature, and oxidative/thermal stability, among other properties, can be measured using DSC.

2.6.3 Applications

DSC is often used in industrial manufacturing, ensuring sample purity and confirming compositional analysis. Also used in materials research, providing information about properties and composition of unknown materials can be determined. DSC has also been used in the food and pharmaceutical industries, providing characterization and enabling the fine-tuning of certain properties. The stability of proteins and folding/unfolding information can also be measured with DSC experiments.

2.6.4 Instrumentation

2.6.4.1 Equipment

The sample and reference cells (also known as pans), each enclosing their respective materials, are contained in an insulated adiabatic chamber (Figure 2.57). The cells can be made of a variety of materials, such as aluminum, copper, gold and platinum. The choice of which is dictated by the necessary upper temperature limit. A variable heating element around each cell transfers heat to the sample, causing both cells' temperature to rise in coordination with the other cell. A temperature monitor measures the temperatures of each cell and a microcontroller controls the variable heating elements and reports the differential power required for heating the sample versus the reference. A typical setup, including a computer for controlling software, is shown in Figure 2.58.

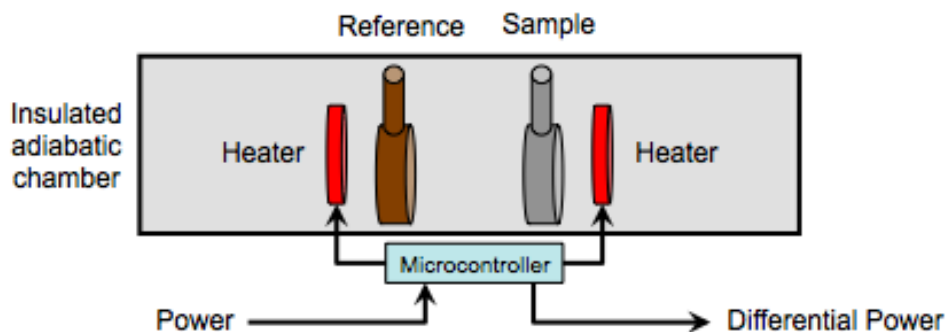


Figure 2.57: Diagram of basic DSC equipment.

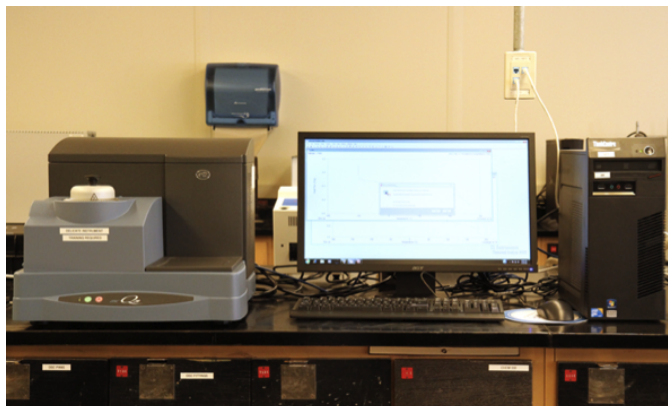


Figure 2.58: Picture of a basic DSC setup in a laboratory.

2.6.4.2 Modes of operations

With advancement in DSC equipment, several different modes of operations now exist that enhance the applications of DSC. Scanning mode typically refers to conventional DSC, which uses a linear increase or decrease in temperature. An example of an additional mode often found in newer DSC equipment is an isothermal scan mode, which keeps temperature constant while the differential power is measured. This allows for stability studies at constant temperatures, particularly useful in shelf life studies for pharmaceutical drugs.

2.6.4.3 Calibration

As with practically all laboratory equipment, calibration is required. Calibration substances, typically pure metals such as indium or lead, are chosen that have clearly defined transition states to ensure that the measured transitions correlate to the literature values.

2.6.5 Obtaining measurements

2.6.5.1 Sample preparation

Sample preparation mostly consists of determining the optimal weight to analyze. There needs to be enough of the sample to accurately represent the material, but the change in heat flow should typically be between 0.1 - 10 mW. The sample should be kept as thin as possible and cover as much of the base of the cell as possible. It is typically better to cut a slice of the sample rather than crush it into a thin layer. The correct reference material also needs to be determined in order to obtain useful data.

2.6.5.2 DSC curves

DSC curves (e.g., Figure 2.59) typically consist of the heat flow plotted versus the temperature. These curves can be used to calculate the enthalpies of transitions, (ΔH), (2.48), by integrating the peak of the state transition, where K is the calorimetric constant and A is the area under the curve.

$$\Delta H = KA \quad (2.48)$$

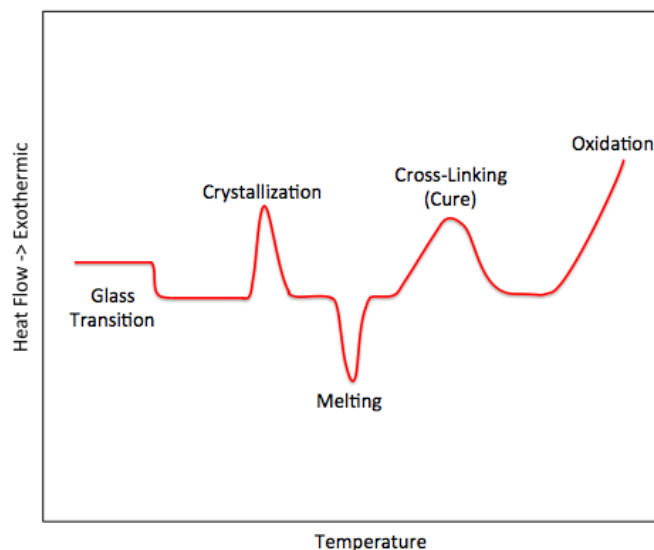


Figure 2.59: An idealized DSC curve showing the shapes associated with particular phase transitions.

2.6.5.3 Sources of error

Common error sources apply, including user and balance errors and improper calibration. Incorrect choice of reference material and improper quantity of sample are frequent errors. Additionally, contamination and how the sample is loaded into the cell affect the DSC.

2.6.6 Bibliography

- E. Watson, M. O'Neill, J. Justin, and N. Brenner, *Anal. Chem.*, 1964, **36**, 1233.
- E. Watson and M. O'Neill, U.S. Patent 3,263,484 (1966).
- G. Hohne, W. Hemminger, and H. Flammersheim, *Differential Scanning Calorimetry*, 2nd Ed, Springer, New York, (2003).
- V. Berstein and V. Egorov, *Differential Scanning Calorimetry of Polymers: Physics, Chemistry, Analysis, Technology*, Ellis Horwood, New York, (1994).
- J. Dean, *The Analytical Chemistry Handbook*; McGraw Hill: New York, (1995).
- E. Gmelin and St. M. Sarge, *Pure Appl. Chem.* 1995, **67**, 1789.

2.7 BET Surface Area Analysis of Nanoparticles ¹⁶

2.7.1 Introduction

In the past few years, nanotechnology research has expanded out of the chemistry department and into the fields of medicine, energy, aerospace and even computing and information technology. With bulk materials, the surface area to volume is insignificant in relation to the number of atoms in the bulk, however when the particles are only 1 to 100 nm across, different properties begin to arise. For example, commercial grade zinc oxide has a surface area range of 2.5 to 12 m²/g while nanoparticle zinc oxide can have surface areas as high as 54 m²/g . The nanoparticles have superior UV blocking properties when compared to the bulk material, making them useful in applications such as sunscreen. Many useful properties of nanoparticles rise from their small size, making it very important to be able to determine their surface area.

2.7.2 Overview of BET theory

The BET theory was developed by Stephen Brunauer (Figure 2.60), Paul Emmett (Figure 2.61), and Edward Teller (Figure 2.62) in 1938. The first letter of each publisher's surname was taken to name this theory. The BET theory was an extension of the Langmuir theory, developed by Irving Langmuir (Figure 2.63) in 1916.



Figure 2.60: Hungarian chemist Stephen Brunauer (1903-1986). Adapted from K. S. Sing, Langmuir, 1987, **3**, 2 (Copyright: American Chemical Society).

¹⁶This content is available online at <<http://cnx.org/content/m38278/1.1/>>.

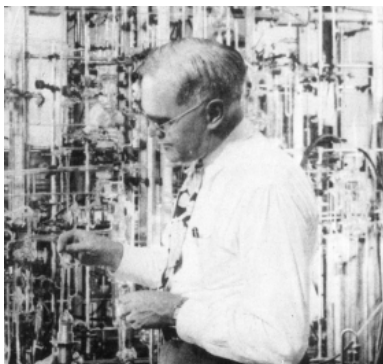


Figure 2.61: American chemical engineer Paul H. Emmett (1900 - 1985). Adapted from B.H. Davis, J. Phys. Chem., 1986, **90**, 4702 (Copyright: American Chemical Society).



Figure 2.62: Hungarian born theoretical physicist Edward Teller (1908 – 2003) shown in 1958 as the director of Lawrence Livermore National Laboratory was known as "the father of the hydrogen bomb".

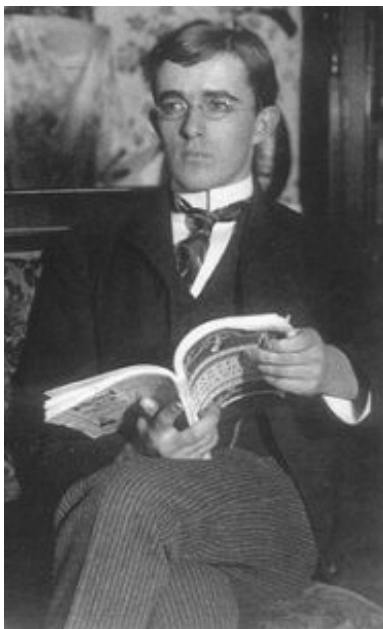


Figure 2.63: American chemist and physicist Irving Langmuir (1881 - 1957). Adapted from *J. Chem. Educ.*, 1933, **10**, 65 (Copyright: American Chemical Society).

The Langmuir theory relates the monolayer adsorption of gas molecules (Figure 2.64), also called adsorbates, onto a solid surface to the gas pressure of a medium above the solid surface at a fixed temperature to (2.49), where θ is the fractional cover of the surface, P is the gas pressure and α is a constant.

$$\theta = \frac{\alpha \cdot P}{1 + (\alpha \cdot P)} \quad (2.49)$$

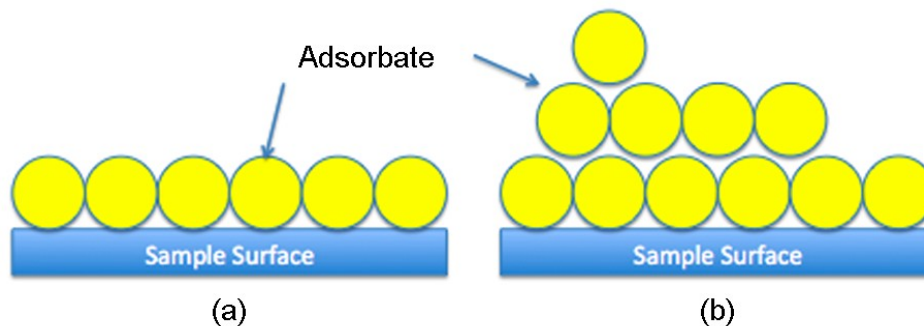


Figure 2.64: Schematic of the adsorption of gas molecules onto the surface of a sample showing (a) the monolayer adsorption model assumed by the Langmuir theory and (b) the multilayer adsorption model assumed by the BET theory.

The Langmuir theory is based on the following assumptions:

- All surface sites have the same adsorption energy for the adsorbate, which is usually argon, krypton or nitrogen gas. The surface site is defined as the area on the sample where one molecule can adsorb onto.
- Adsorption of the solvent at one site occurs independently of adsorption at neighboring sites.
- Activity of adsorbate is directly proportional to its concentration.
- Adsorbates form a monolayer.
- Each active site can be occupied only by one particle.

The Langmuir theory has a few flaws that are addressed by the BET theory. The BET theory extends the Langmuir theory to multilayer adsorption (Figure 2.64) with three additional assumptions:

- Gas molecules will physically adsorb on a solid in layers infinitely.
- The different adsorption layers do not interact.
- The theory can be applied to each layer.

2.7.3 How does BET work?

Adsorption is defined as the adhesion of atoms or molecules of gas to a surface. It should be noted that adsorption is not confused with absorption, in which a fluid permeates a liquid or solid. The amount of gas adsorbed depends on the exposed surface area but also on the temperature, gas pressure and strength of interaction between the gas and solid. In BET surface area analysis, nitrogen is usually used because of its availability in high purity and its strong interaction with most solids. Because the interaction between gaseous and solid phases is usually weak, the surface is cooled using liquid N_2 to obtain detectable amounts of adsorption. Known amounts of nitrogen gas are then released stepwise into the sample cell. Relative pressures less than atmospheric pressure is achieved by creating conditions of partial vacuum. After the saturation pressure, no more adsorption occurs regardless of any further increase in pressure. Highly precise and accurate pressure transducers monitor the pressure changes due to the adsorption process. After the adsorption layers are formed, the sample is removed from the nitrogen atmosphere and heated to cause the adsorbed nitrogen to be released from the material and quantified. The data collected is displayed in the form of a BET isotherm, which plots the amount of gas adsorbed as a function of the relative pressure. There are five types of adsorption isotherms possible.

2.7.3.1 Type I isotherm

Type I is a pseudo-Langmuir isotherm because it depicts monolayer adsorption (Figure 2.65). A type I isotherm is obtained when $P/P_o < 1$ and $c > 1$ in the BET equation, where P/P_o is the partial pressure value and c is the BET constant, which is related to the adsorption energy of the first monolayer and varies from solid to solid. The characterization of microporous materials, those with pore diameters less than 2 nm, gives this type of isotherm.

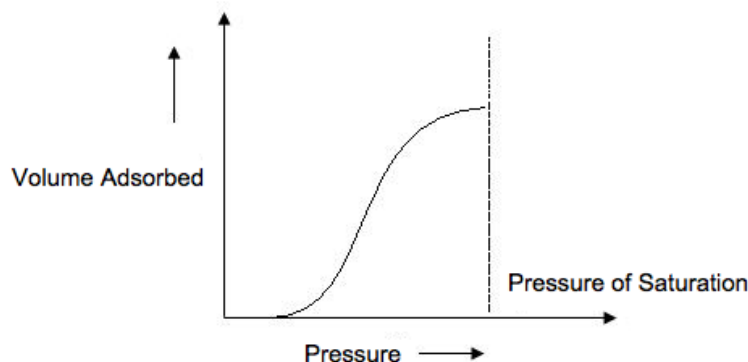


Figure 2.65: The isotherm plots the volume of gas adsorbed onto the surface of the sample as pressure increases. Adapted from S. Brunauer L. S. Deming, W. E. Deming, and E. Teller, *J. Am. Chem. Soc.*, 1940, **62**, 1723.

2.7.3.2 Type II isotherm

A type II isotherm (Figure 2.66) is very different than the Langmuir model. The flatter region in the middle represents the formation of a monolayer. A type II isotherm is obtained when $c > 1$ in the BET equation. This is the most common isotherm obtained when using the BET technique. At very low pressures, the micropores fill with nitrogen gas. At the knee, monolayer formation is beginning and multilayer formation occurs at medium pressure. At the higher pressures, capillary condensation occurs.

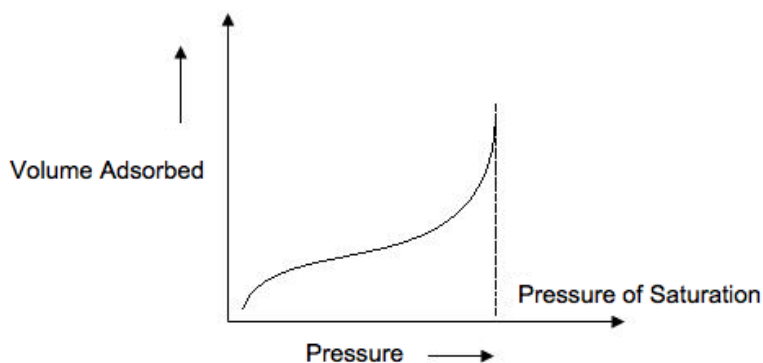


Figure 2.66: The isotherm plots the volume of gas adsorbed onto the surface of the sample as pressure increases. Adapted from S. Brunauer, L. S. Deming, W. E. Deming, and E. Teller, *J. Am. Chem. Soc.*, 1940, **62**, 1723.

2.7.3.3 Type III isotherm

A type III isotherm (Figure 2.67) is obtained when the $c < 1$ and shows the formation of a multilayer. Because there is no asymptote in the curve, no monolayer is formed and BET is not applicable.

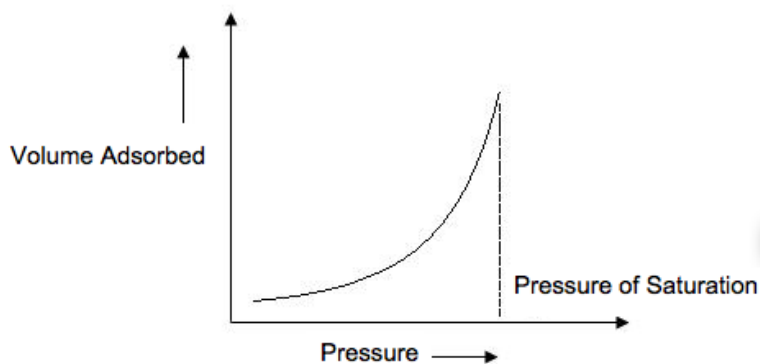


Figure 2.67: Brunauer, L. S. Deming, W. E. Deming, and E. Teller, *J. Am. Chem. Soc.*, 1940, **62**, 1723.

2.7.3.4 Type IV isotherm

Type IV isotherms (Figure 2.68) occur when capillary condensation occurs. Gases condense in the tiny capillary pores of the solid at pressures below the saturation pressure of the gas. At the lower pressure regions, it shows the formation of a monolayer followed by a formation of multilayers. BET surface area characterization of mesoporous materials, which are materials with pore diameters between 2 - 50 nm, gives this type of isotherm.

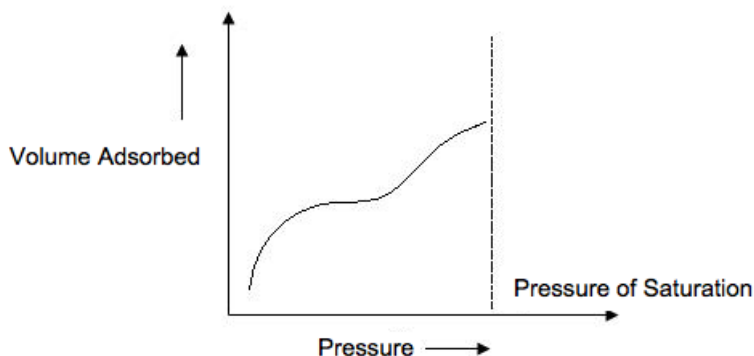


Figure 2.68: Brunauer, L. S. Deming, W. E. Deming, and E. Teller, *J. Am. Chem. Soc.*, 1940, **62**, 1723.

2.7.3.5 Type V isotherm

Type V isotherms (Figure 2.69) are very similar to type IV isotherms and are not applicable to BET.

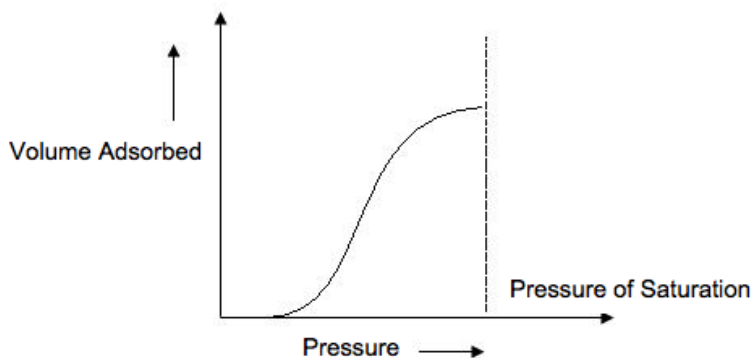


Figure 2.69: Brunauer L. S. Deming, W. E. Deming, and E. Teller, *J. Am. Chem. Soc.*, 1940, **62**, 1723.

2.7.4 Calculations

The BET equation, (2.50), uses the information from the isotherm to determine the surface area of the sample, where X is the weight of nitrogen adsorbed at a given relative pressure (P/P_0), X_m is monolayer capacity, which is the volume of gas adsorbed at standard temperature and pressure (STP), and C is constant. STP is defined as 273 K and 1 atm.

$$\frac{1}{X[(P_0/P)-1]} = \frac{1}{X_m C} + \frac{C-1}{X_m C} \left(\frac{P}{P_0} \right) \quad (2.50)$$

2.7.4.1 Multi-point BET

Ideally five data points, with a minimum of three data points, in the P/P_0 range 0.025 to 0.30 should be used to successfully determine the surface area using the BET equation. At relative pressures higher than 0.5, there is the onset of capillary condensation, and at relative pressures that are too low, only monolayer formation is occurring. When the BET equation is plotted, the graph should be of linear with a positive slope. If such a graph is not obtained, then the BET method was insufficient in obtaining the surface area.

- The slope and y-intercept can be obtained using least squares regression.
- The monolayer capacity X_m can be calculated with (2.51).
- Once X_m is determined, the total surface area S_t can be calculated with the following equation, where L_{av} is Avogadro's number, A_m is the cross sectional area of the adsorbate and equals 0.162 nm^2 for an adsorbed nitrogen molecule, and M_v is the molar volume and equals 22414 mL, (2.52).

$$X_m = \frac{1}{s + i} = \frac{C - 1}{Cs} \quad (2.51)$$

$$S = \frac{X_m L_{av} A_m}{M_v} \quad (2.52)$$

Single point BET can also be used by setting the intercept to 0 and ignoring the value of C . The data point at the relative pressure of 0.3 will match up the best with a multipoint BET. Single point BET can be used over the more accurate multipoint BET to determine the appropriate relative pressure range for multi-point BET.

2.7.5 Sample preparation and experimental setup

Prior to any measurement the sample must be degassed to remove water and other contaminants before the surface area can be accurately measured. Samples are degassed in a vacuum at high temperatures. The highest temperature possible that will not damage the sample's structure is usually chosen in order to shorten the degassing time. IUPAC recommends that samples be degassed for at least 16 hours to ensure that unwanted vapors and gases are removed from the surface of the sample. Generally, samples that can withstand higher temperatures without structural changes have smaller degassing times. A minimum of 0.5 g of sample is required for the BET to successfully determine the surface area.

Samples are placed in glass cells to be degassed and analyzed by the BET machine. Glass rods are placed within the cell to minimize the dead space in the cell. Sample cells typically come in sizes of 6, 9 and 12 mm and come in different shapes. 6 mm cells are usually used for fine powders, 9 mm cells for larger particles and small pellets and 12 mm are used for large pieces that cannot be further reduced. The cells are placed into heating mantles and connected to the outgas port of the machine.

After the sample is degassed, the cell is moved to the analysis port (Figure 2.70). Dewars of liquid nitrogen are used to cool the sample and maintain it at a constant temperature. A low temperature must be

maintained so that the interaction between the gas molecules and the surface of the sample will be strong enough for measurable amounts of adsorption to occur. The adsorbate, nitrogen gas in this case, is injected into the sample cell with a calibrated piston. The dead volume in the sample cell must be calibrated before and after each measurement. To do that, helium gas is used for a blank run, because helium does not adsorb onto the sample.

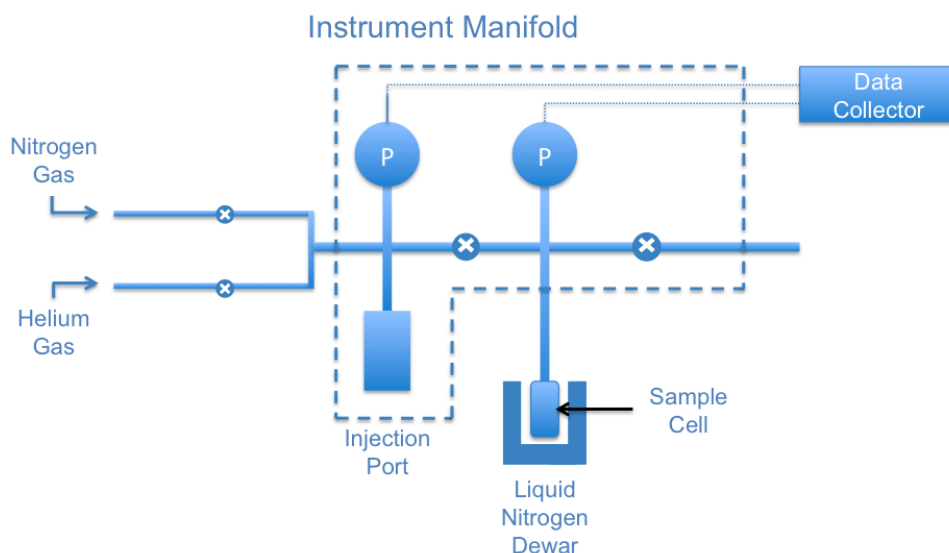


Figure 2.70: Schematic representation of the BET instrument. The degasser is not shown.

2.7.6 Shortcomings of BET

The BET technique has some disadvantages when compared to NMR, which can also be used to measure the surface area of nanoparticles. BET measurements can only be used to determine the surface area of dry powders. This technique requires a lot of time for the adsorption of gas molecules to occur. A lot of manual preparation is required.

2.7.7 The surface area determination of metal-organic frameworks

The BET technique was used to determine the surface areas of metal-organic frameworks (MOFs), which are crystalline compounds of metal ions coordinated to organic molecules. Possible applications of MOFs, which are porous, include gas purification and catalysis. An isoreticular MOF (IRMOF) with the chemical formula $\text{Zn}_4\text{O}(\text{pyrene-1,2-dicarboxylate})_3$ (Figure 2.71) was used as an example to see if BET could accurately determine the surface area of microporous materials. The predicted surface area was calculated directly from the geometry of the crystals and agreed with the data obtained from the BET isotherms. Data was collected at a constant temperature of 77 K and a type II isotherm (Figure 2.72) was obtained.

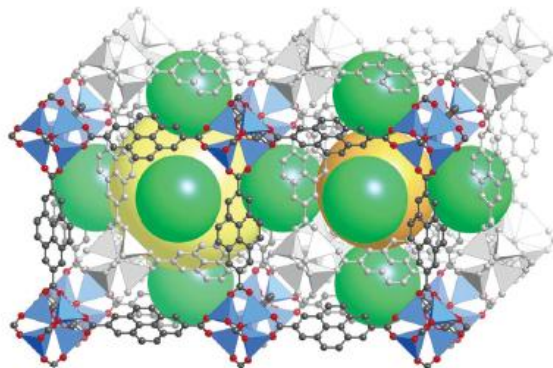


Figure 2.71: The structure of catenated IRMOF-13. Orange and yellow represent non-catenated pore volumes. Green represents catenated pore volume.

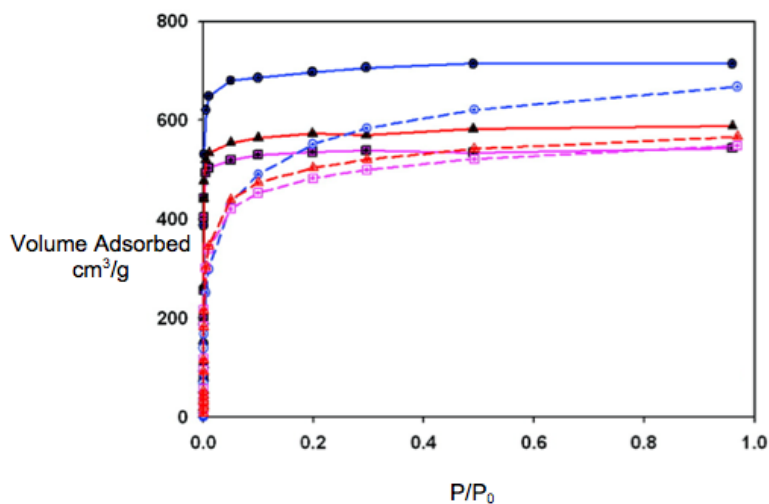


Figure 2.72: The BET isotherms of the zeolites and metal-organic frameworks. IRMOF-13 is symbolized by the black triangle and red line. Adapted from Y.S. Bae, R.Q. Snurr, and O. Yazaydin, *Langmuir*, 2010, **26**, 5478.

The isotherm data obtained from partial pressure range of 0.05 to 0.3 is plugged into the BET equation, (2.50), to obtain the BET plot (Figure 2.73).

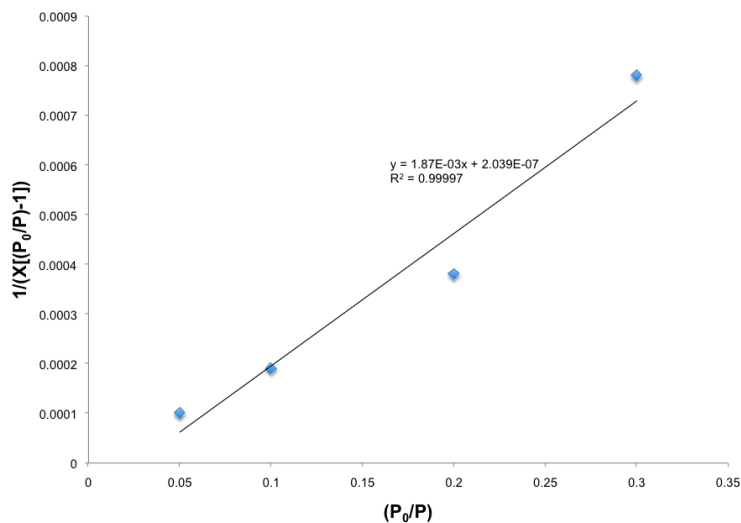


Figure 2.73: BET plot of IRMOF-13 using points collected at the pressure range 0.05 to 0.3. The equation of the best-fit line and R^2 value are shown. Adapted from Y.S. Bae, R.Q. Snurr, and O. Yazaydin, *Langmuir*, 2010, **26**, 5479.

Using (2.53), the monolayer capacity is determined to be $391.2 \text{ cm}^3/\text{g}$.

$$X_m = \frac{1}{(2.66E-3) + (-5.512E-05)} \quad (2.53)$$

Now that X_m is known, then (2.54) can be used to determine that the surface area is $1702.3 \text{ m}^2/\text{g}$.

$$S = \frac{391.2 \text{ cm}^3 * 0.162 \text{ nm}^2 * 6.02 * 10^{23}}{22.414 \text{ L}} \quad (2.54)$$

2.7.8 Bibliography

- B. H. Davis, *J. Phys. Chem.*, 1986, **90**, 4702.
- K. S. Sing, *Langmuir*, 1987, **3**, 2.
- *Brunauer-Emmett-Teller (BET) Surface Area Analysis and Barrett-Joyner-Halenda (BJH) Pore Size and Volume Analysis*, Testing and Analysis Techniques. CERAM.
- S. Brunauer, L. S. Deming, W. E. Deming, and E. Teller, *J. Am. Chem. Soc.*, 1940, **62**, 1723.
- S. Brunauer, P. H. Emmett, and E. Teller, *J. Am. Chem. Soc.*, 1938, **60**, 309.
- Y. S. Bae, R. Q. Snurr, and O. Yazaydin, *Langmuir*, 2010, **26**, 5475.

2.8 Introduction to Cyclic Voltammetry Measurements ¹⁷

2.8.1 Introduction

Cyclic voltammetry (CV) is one type of potentiodynamic electrochemical measurements. Generally speaking, the operating process is a potential-controlled reversible experiment, which scans the electric potential before turning to reverse direction after reaching the final potential and then scans back to the initial potential, as shown in Figure 2.74a. When voltage is applied to the system changes with time, the current will change with time accordingly as shown in Figure 2.74b. Thus the curve of current and voltage, illustrated in Figure 2.74c, can be represented from the data, which can be obtained from Figure 2.74a and b.

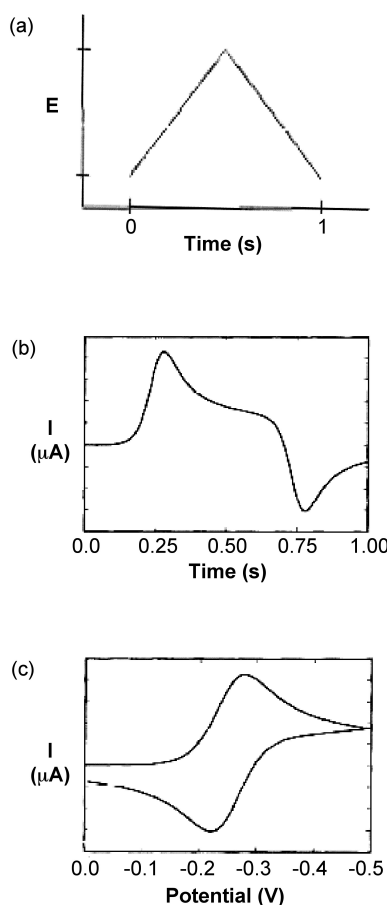


Figure 2.74: Potential wave changes with time (a); current response with time (b); current-potential representations (c). Adapted from D. K. Gosser, Jr. *Cyclic Voltammetry Simulation and Analysis of Reaction Mechanisms*, Wiley-VCH, New York, (1993).

Cyclic voltammetry is a very important analytical characterization in the field of electrochemistry. Any process that includes electron transfer can be investigated with this characterization. For example, the

¹⁷This content is available online at <http://cnx.org/content/m34669/1.1/>.

investigation of catalytical reactions, analyzing the stoichiometry of complex compounds, and determining of the photovoltaic materials' band gap. In this module, I will focus on the application of CV measurement in the field of characterization of solar cell materials.

Although CV was first practiced using a hanging mercury drop electrode, based on the work of Nobel Prize winner Heyrovský (Figure 2.75), it did not gain widespread until solid electrodes like Pt, Au and carbonaceous electrodes were used, particularly to study anodic oxidations. A major advance was made when mechanistic diagnostics and accompanying quantitations became known through the computer simulations. Now, the application of computers and related software packages make the analysis of data much quicker and easier.



Figure 2.75: Czech chemist and inventor Jaroslav Heyrovský (1890 – 1967).

2.8.2 The components of a CV system

As shown in Figure 2.76, the CV systems are as follows:

- The epsilon includes potentiostat and current-voltage converter. The potentiostat is required for controlling the applied potential, and a current-to-voltage converter is used for measuring the current, both of which are contained within the epsilon (Figure 2.76).
- The input system is a function generator (Figure 2.76). Operators can change parameters, including scan rate and scan range, through this part. The output part is a computer screen, which can show data and curves directly to the operators.
- All electrodes must work in electrolyte solution (Figure 2.76).
- Sometimes, the oxygen and water in the atmosphere will dissolve in the solution, and will be deoxidized or oxidized when voltage is applied. Therefore the data will be less accurate. To prevent this from happening, bubbling of an inert gas (nitrogen or argon) is required.
- The key component of the CV systems is the electrochemical cell (Figure 2.76), which is connected to the epsilon part. Electrochemical cell contains three electrodes, counter electrode (C in Figure 2.76), working electrode (W in Figure 2.76) and reference electrode (R in Figure 2.76). All of them must be immersed in an electrolyte solution when working.

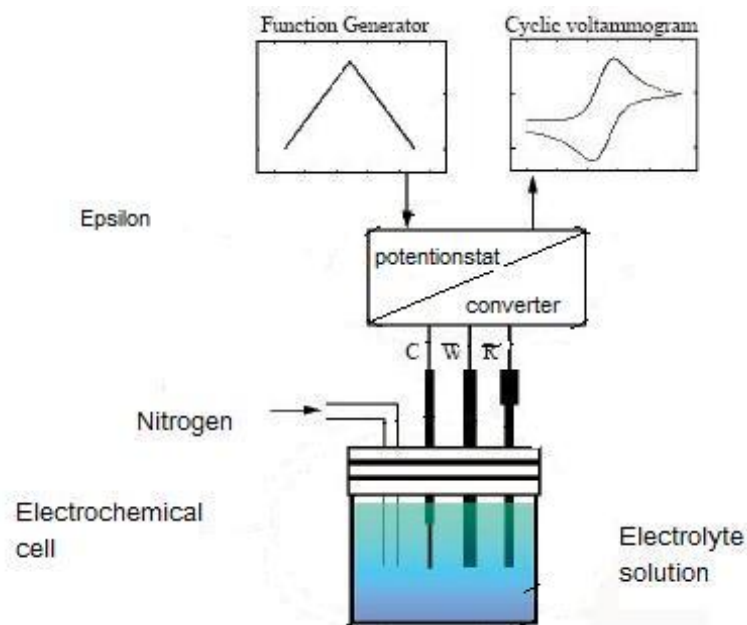


Figure 2.76: Components of cyclic voltammetry systems. Adapted from D. K. Gosser, Jr., *Cyclic Voltammetry Simulation and Analysis of Reaction Mechanisms*, Wiley-VCH, New York, (1993).

In order to better understand the electrodes mentioned above, three kinds of electrodes will be discussed in more detail.

- Counter electrodes (C in Figure 2.76) are non-reactive high surface area electrodes, for which the platinum gauze is the common choice.
- The working electrode (W in Figure 2.76) is commonly an inlaid disc electrodes (Pt, Au, graphite, etc.) of well-defined area are most commonly used. Other geometries may be available in appropriate circumstances, such as dropping or hanging mercury hemisphere, cylinder, band, arrays, and grid electrodes.
- For the reference electrode (R in Figure 2.76), aqueous Ag/AgCl or calomel half cells are commonly used, and can be obtained commercially or easily prepared in the laboratory. Sometimes, a simple silver or platinum wire is used in conjunction with an internal potential reference provided by ferrocene (Figure 2.77), when a suitable conventional reference electrode is not available. Ferrocene undergoes a one-electron oxidation at a low potential, around 0.5 V versus a saturated calomel electrode (SCE). It is also been used as standard in electrochemistry as $F_c^+/F_c = 0.64$ V versus a normal hydrogen electrode (NHE).

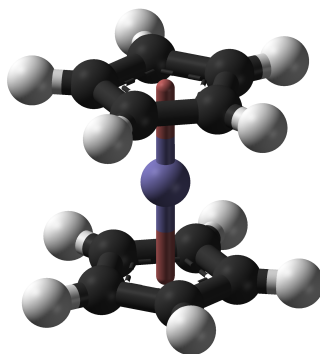


Figure 2.77: The structure of $(C_5H_5)_2Fe$ (ferrocene).

Cyclic voltammetry systems employ different types of potential waveforms (Figure 2.78) that can be used to satisfy different requirements. Potential waveforms reflect the way potential is applied to this system. These different types are referred to by characteristic names, for example, cyclic voltammetry, and differential pulse voltammetry. The cyclic voltammetry analytical method is the one whose potential waveform is generally an isosceles triangle (Figure 2.78a).

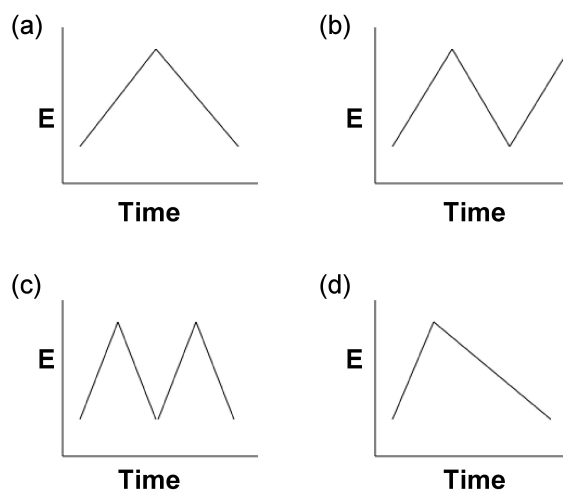


Figure 2.78: Examples of different waveforms of CV systems, illustrating various possible cycles. Adapted from D. K. Gosser, Jr., *Cyclic Voltammetry Simulation and Analysis of Reaction Mechanisms*, Wiley-VCH, New York (1993).

2.8.3 The physical principles on which the CV systems are based

As mentioned above, there are two main parts of a CV system: the electrochemical cell and the epsilon. Figure 2.79 shows the schematic drawing of circuit diagram in electrochemical cell.

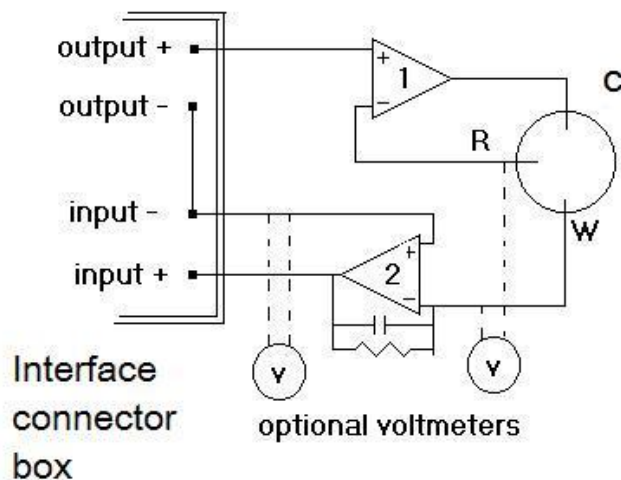


Figure 2.79: Diagram of a typical cyclic voltammetry circuit layout. Adapted from R. G. Compton and C. E. Banks, *Understanding Voltammetry*, World Scientific, Singapore (2007).

In a voltammetric experiment, potential is applied to a system, using working electrode (W in Figure 2.79) and the reference electrode (R = Figure 2.79), and the current response is measured using the working electrode and a third electrode, the counter electrode (C in Figure 2.79). The typical current-voltage curve for ferricyanide/ferrocyanide, (2.55), is shown in Figure 2.80.



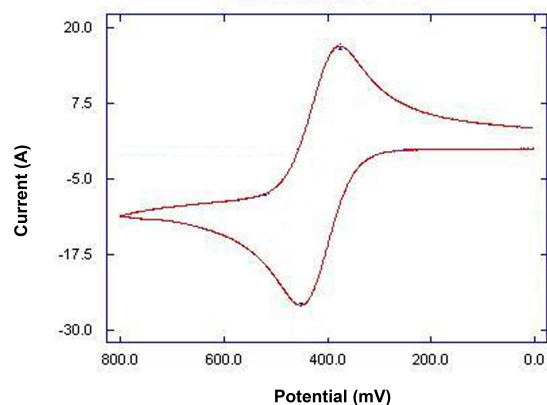


Figure 2.80: Typical curve of current-voltage curve for for ferricyanide/ferrocyanide, (2.55).

2.8.3.1 What useful information we can get from the data collected

The information we are able to obtain from CV experimental data is the current-voltage curve. From the curve we can then determine the redox potential, and gain insights into the kinetics of electron reactions, as well as determine the presence of reaction intermediate.

2.8.4 Why choose CV for the characterizations of solar cell materials?

Despite some limitations, cyclic voltammetry is very well suited for a wide range of applications. Moreover, in some areas of research, cyclic voltammetry is one of the standard techniques used for characterization. Due to its characteristic shapes of curves, it has been considered as 'electrochemical spectroscopy'. In addition, the system is quite easy to operate, and sample preparation is relatively simple.

The band gap of a semiconductor is a very important value to be determined for photovoltaic materials. Figure 2.81 shows the relative energy level involved in light harvesting of an organic solar cell. The energy difference (E_g) between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO), which determines the efficiency. The oxidation and reduction of an organic molecule involve electron transfers (Figure 2.82), and CV measurements can be used to determine the potential change during redox. Through the analysis of data obtained by the CV measurement the electronic band gap is obtained.

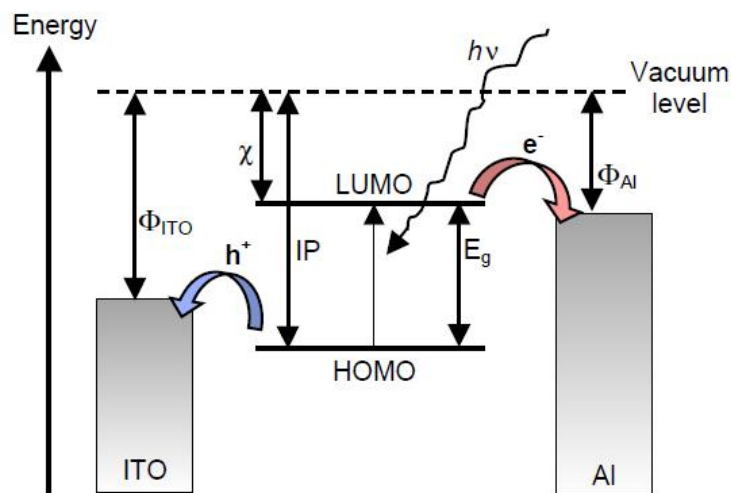


Figure 2.81: Diagram showing energy level and light harvesting of an organic solar cell. Adapted from S. B. Darling, *Energy Environm. Sci.*, 2009, 2, 1266.

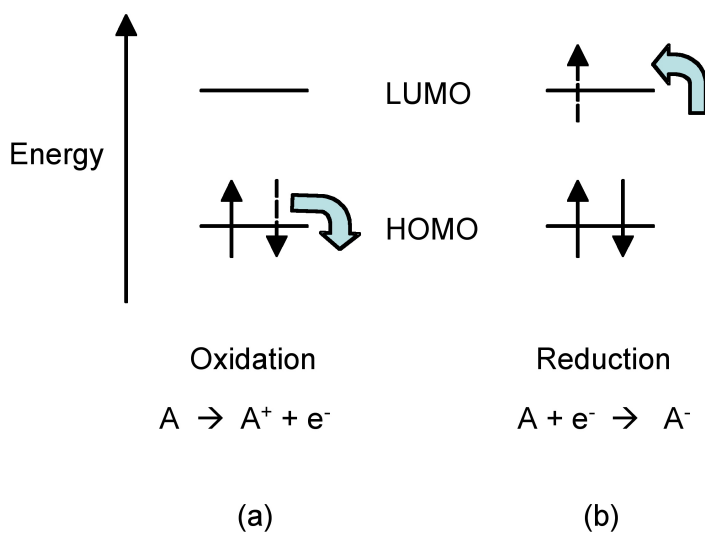


Figure 2.82: Diagram showing energy level and light harvesting of organic solar cell. Adapted from D. K. Gosser, Jr., *Cyclic Voltammetry Simulation and Analysis of Reaction Mechanisms*, Wiley-VCH, New York (1993).

2.8.4.1 The example of the analysis of CV data in solar cell material characterization

Graphene nanoribbons (GNRs) are long, narrow sheets of graphene formed from the unzipping of carbon nanotubes (Figure 2.83). GNRs can be both semiconducting and semi-metallic, depending on their width, and they represent a particularly versatile variety of graphene. The high surface area, high aspect ratio, and interesting electronic properties of GNRs render them promising candidates for applications of energy-storage materials.

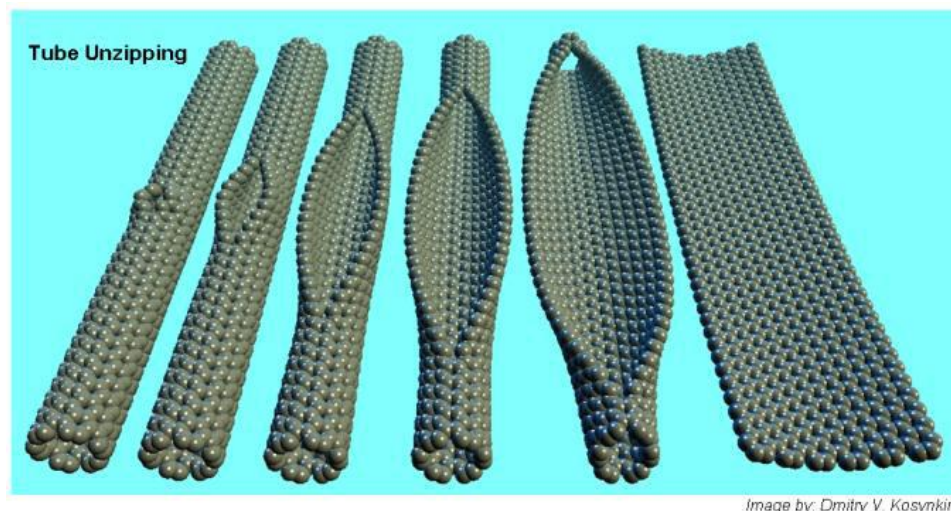


Figure 2.83: Schematic for the “unzipping” of carbon nanotubes to produce graphene (Rice University).

Graphene nanoribbons can be oxidized to oxidized graphene nanoribbons (XGNRs), are readily soluble in water easily. Cyclic voltammetry is an effective method to characterize the band gap of semiconductor materials. To test the band gap of oxidized graphene nanoribbons (XGNRs), operating parameters can be set as follows:

- 0.1M KCl solution
- Working electrode: evaporated gold on silicon.
- Scan rate: 10 mV/s.
- Scan range: 0 ~ 3000 mV for oxidization reaction; -3000 ~ 0 mV for reduction reaction.
- Samples preparation: spin coat an aqueous solution of the oxidized graphene nanoribbons onto the working electrode, and dry at 100 °C.

To make sure that the results are accurate, two samples can be tested under the same condition to see whether the redox peaks are at the same position. The amount of XGNRs will vary from sample to sample, thus the height of peaks will vary also. Typical curves obtained from the oxidation reaction (Figure 2.82a) and reduction reaction (Figure 2.82b) are shown in Figure 2.84 and Figure 2.85, respectively.

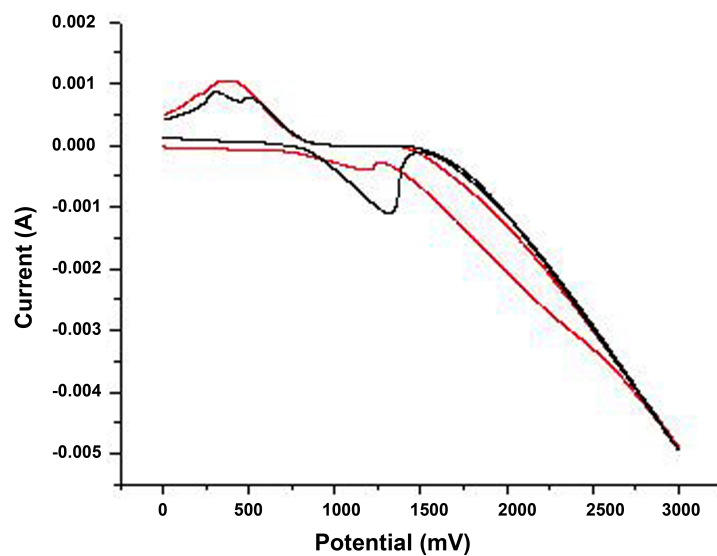


Figure 2.84: Oxidation curves of two samples of XGNRs prepared under similar condition. The sample with lower concentration is shown by the red curve, while the sample with higher concentration is shown as a black curve.

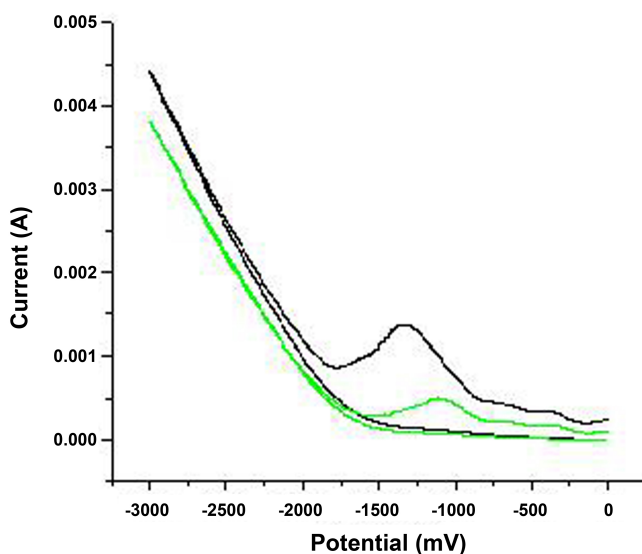


Figure 2.85: Reduction curves of two samples of XGNRs prepared under similar condition. The sample with lower concentration is shown by the green curve, while the sample with higher concentration is shown as a black curve.

From the curves shown in Figure 2.84 and Figure 2.85 the following conclusions can be obtained:

- Two reduction peak and onset is about -0.75 V (i.e., Figure 2.82b).
- One oxidation peak with onset about 0.85 V (i.e., Figure 2.82a).
- The calculated band gap = 1.60 eV.

In conclusion, there are many applications for CV system, efficient method, and the application in the field of solar cell provides the band gap information for research.

2.8.5 Bibliography

- R. N. Adams, *Electrochemistry at Solid Electrodes*, Marcel Dekker, NewYork (1968).
- R. G. Compton, and C. E. Banks, *Understanding Voltammetry*, World Scientific, Singapore, (2007).
- S. B. Darling, *Energy Environm. Sci.*, 2009, **2**, 1266.
- S. W. Feldberg, *A General Method for Simulation*, Vol. 3 in Electroanalytical Chemistry Series, Marcel Dekker, NewYork, (1969).
- W. Kemula and Z. Kublik, *Nature*, 1958, **182**, 793.
- D. V. Kosynkin, A. L Higginbotham, A. Sinitskii, J. R. Lomeda, A. Dimiev, B. K. Price, and J. M. Tour, *Nature*, 2009, **458**, 872.
- R. S. Nicholson and I. Shain, *Anal. Chem.*, 1964, **36**, 706.
- L. Piszczek, A. Lgnatowicz, J. Kielbase, *J. Chem. Edu.*, 1998, **65**, 171.
- J. Zhu, Z. Zhao, D. Xiao, J. Li, X. Yang, and Y. Wu, *Electrochem. Commun.*, 2005, **7**, 58.

2.9 Determination of Relaxation Parameters of Contrast Agents ¹⁸

2.9.1 Introduction

Magnetic resonance imaging (MRI) (also known as nuclear magnetic resonance imaging (NMRI) or magnetic resonance tomography (MRT)) is a powerful noninvasive diagnostic technique, which is used to generate magnetic field (B_0) and interacts with spin angular momentum of the nucleus in the tissue. Spin angular momentum depends on number of protons and neutrons of nucleus. Nuclei with even number of protons plus neutrons are insensitive to magnetic field, so cannot be viewed by MRI.

Each nucleus can be considered as an arrow with arbitrary direction in absence of external magnetic field (Figure 2.86). And we consider them to get oriented in same direction once magnetic field applied (Figure 2.87). In order to get nuclei orient in specific direction, energy is supplied, and to bring it to original position energy is emitted. All this transitions eventually lead to changes in angular velocity, which is defined as Larmor frequency and the expression (2.56), where ω is the Larmor frequency, γ is the gyromagnetic ratio, and B_0 is the magnetic field. It is not easy to detect energy, which is involved in such a transition, that's why use of high resolution spectrometers required, those which are developed by nowadays as a most powerful MRI are close to 9 Tesla with mass approaching forty five tons. Unfortunately it is expensive tool to purchase and to operate. That's why new techniques should be developed, so most of the MRI spectrometers can be involved in imaging. Fortunately presence of huge amount of nuclei in analyzed sample or body can provide with some information.

$$\omega = \gamma B_0 \quad (2.56)$$

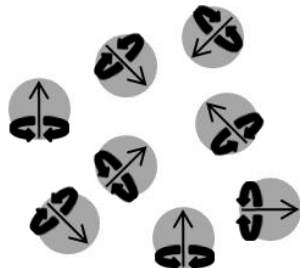


Figure 2.86: Representation of nuclei in absence of magnetic field.

¹⁸This content is available online at <<http://cnx.org/content/m38342/1.1/>>.

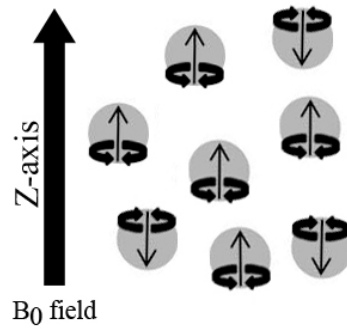


Figure 2.87: Representation of nuclei in presence of magnetic field.

2.9.1.1 Nuclear magnetic resonance relaxometer

Each nucleus possesses microscopic magnetic spins of x , y and z . Presence of randomly distributed atoms with varying x and y spins will lead to zero upon summation of x and y planes. But in case of z , summation of magnetic spins will not lead to cancellation. According to Curie's law, (2.57), (M_z is the resulting magnetization of z axis, C is a material specific Curie constant, B_0 is the magnetic field, and T is absolute temperature), magnetization of z axis proportional to magnetic field applied from outside. Basically, excitation happens by passing current through coil which leads to magnetization of x , y and z axis. It is the way of changing magnetism from z axis to x and y axis. Once external current supply is turned off, magnetization will eventually quench. This means a change of magnetization from x and y axis to z axis, were it eventually become equilibrated and device no more can detect the signals. Energy which is emitted from excited spin leads to development of new current inside of the same coil recorded by detector; hence same coil can be used as detector and source of magnetic field. This process called as a relaxation and that's why, return of magnetization to z axis called as spin-lattice relaxation or T_1 relaxation (time required for magnetization to align on z axis). Eventual result of zero magnetization on x and y axis called as spin-spin relaxation or T_2 relaxation (Figure 2.88).

$$M_z = CB_0/T \quad (2.57)$$

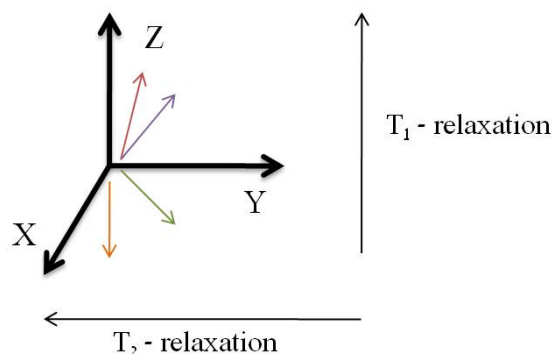


Figure 2.88: Magnetic spins relaxation mechanism

2.9.2 Contrast agents for MRI

In MRI imaging contrast is determined according to T_1 , T_2 or the proton density parameter. Therefore we can obtain three different images. By changing intervals between radio frequency (RF) 90° pulses and RF 180° pulses, the desired type of image can be obtained. There are few computational techniques available to improve contrast of image; those are repetitive scans and different mathematical computations. Repetitive scans take a long time, therefore cannot be applied in MRI. Mathematical computation on their own, do not provide with desired results. For that reason, in order to obtain high resolution images, contrast agents (CA) are an important part of medical imaging.

2.9.2.1 Types of contrast agents

There are different types of contrast agents available in markets which reduce the supremacy of T_1 or T_2 , and differentiate according to relaxivity₁ (r_1) and relaxivity₂ (r_2) values. The relaxivity (r_1) can be described as $1/T_1$ (s^{-1}) of water molecules per mM concentration of CA. Contrast agents are paramagnetic and can interact with dipole moments of water molecules, causing fluctuations in molecules. This theory is known as Solomon-Bloembergen-Morgan (SBM) theory. Those which are efficient were derivatives of gadolinium (e.g., gadobenic acid (FIGURE a) and gadoxetic acid (FIGURE b)), iron (e.g., superparamagnetic iron oxide and ultrasmall superparamagnetic iron oxide) and manganese (e.g., manganese dipyridoxal diphosphate). Fundamentally the role of contrast agents can be played by any paramagnetic species.

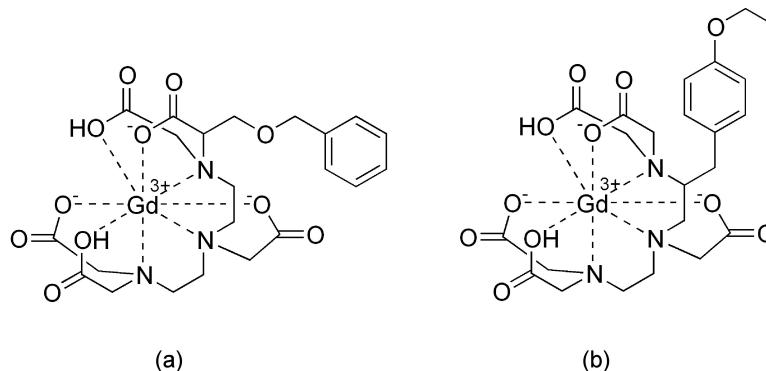


Figure 2.89: The structures of two representative commercial gadolinium MRI contrast agents; (a) gadobenic acid and (b) gadoxetic acid.

2.9.2.2 Principal of interactions of CA with surrounding media

There are two main principles of interactions of contrast agents with water molecules. One is direct interaction, which is called inner sphere relaxation, and the other mechanism that happens in the absence of direct interaction with water molecule which is outer sphere relaxation. If we have water molecules in the first coordination sphere of metal ion, we can consider them as the inner sphere, and if diffusion of protons from outside happens randomly we define them as outer sphere relaxation. Another type of relaxivity comes from already affected water molecules, which transfers their relaxivity to protons of close proximity, this type of relaxivity called second sphere and is usually neglected or contributed as outer sphere. In inner sphere proton relaxivity there are two main mechanisms involved in relaxation. One is dipole-dipole interactions between metal and proton and another is scalar mechanism. Dipole-dipole interaction affects electron spin vectors and scalar mechanism usually controls water exchange. Effect of contrast agents on T_1 relaxation is much larger than on T_2 , since T_1 is much larger for tissues than T_2 .

2.9.3 Determination of relaxivity

Determination of relaxivity became very easy with the advancements of NMR and computer technology, where you need just to load your sample and read values from the screen. But let's consider in more detail what are the precautions should be taken during sample preparation and data acquisition.

2.9.3.1 Sample preparation

The sample to be analyzed is dissolved in water or another solvent. Generally water is used since contrast agents for medical MRI are used in aqueous media. The amount of solution used is determined according to the internal standard volume, which is used for calibration purposes of device and is usually provided by company producing device. A suitable sample holder is a NMR tube. It is important to degas solvent prior measurements by bubbling gas through it (nitrogen or argon works well), so no any traces of oxygen remains in solution, since oxygen is paramagnetic.

2.9.3.2 Data acquisition

Before collecting data it is better to keep the sample in the device compartment for few minutes, so temperature of magnet and your solution equilibrates. The relaxivity (r_i) calculated according to ((2.58)), where T_i is the relaxation time in the presence of CAs, T_{id} is the relaxation time in the absence of CAs, and CA is the concentration of paramagnetic CAs (mM). Having the relaxivity values allows for a comparison of a particular compound to other known contrast agents.

$$r_i = (1/T_i - 1/T_{id})/[CA] \quad (2.58)$$

2.9.4 Bibliography

- D. Canet, *Nuclear Magnetic Resonance: Concepts and Methods*, John Wiley and Sons, Chichester (1996).
- A. Abragam, *Principles of Nuclear Magnetism*, Oxford University Press, Oxford (1961).
- I. Solomon and N. Bloembergen, *J. Chem. Phys.*, 1956, **25**, 261.
- N. Bloembergen and L. O. Morgan, *J. Chem. Phys.*, 1961, **34**, 842.
- P. G. Morris and P. Mansfield, *NMR Imaging in Biomedicine*, Academic Press, Orlando (1982).
- J. S. Ananta, B. Godin, R. Sethi, L. Moriggi, X. Liu, R. E. Serda, R. Krishnamurthy, R. Muthupillai, R. D. Bolskar, L. Helm, M. Ferrari, L. J. Wilson, and P. Decuzzi, *Nature Nanotech.*, 2010, **5**, 817.
- R. B. Lauffer, *Chem. Rev.*, 1987, **87**, 901.

Solutions to Exercises in Chapter 2

Solution to Exercise 2.2.1 (p. 129)

$$m = \Delta T_f / K_f \text{ water} \quad (2.59)$$

$$m = 0.445 \text{ }^\circ\text{C} / 1.86 \text{ }^\circ\text{C.kg/mol} \quad (2.60)$$

$$m = 0.239 \text{ mol} \quad (2.61)$$

Solution to Exercise 2.2.2 (p. 129)

$$M_w = K_f (\text{g solute}) / \Delta T_f (\text{kg solvent}) \quad (2.62)$$

$$M_w = \frac{1.86 \text{ }^\circ\text{C.kg/moles (1.200 g)}}{0.445 \text{ }^\circ\text{C (0.03056 kg)}} \quad (2.63)$$

$$M_w = 164 \text{ g/mol} \quad (2.64)$$

Solution to Exercise 2.2.3 (p. 129)

$$\Delta T_f = K_f(m)i \quad (2.65)$$

$$\Delta T_f = 1.86 \text{ }^\circ\text{C.kg/moles} \times 0.500 \text{ molal} \times 3 \quad (2.66)$$

$$\Delta T_f = 2.79 \text{ }^\circ\text{C} \quad (2.67)$$

Solution to Exercise 2.2.4 (p. 129)

$$g (\text{solute}) = M_w \times \Delta T_f \times (\text{kg solvent}) / K_f \quad (2.68)$$

$$g (\text{solute}) = \frac{164.0 \text{ g/mol (2.79 }^\circ\text{C) 0.06 kg}}{1.86 \text{ }^\circ\text{C.kg/moles}} \quad (2.69)$$

$$g (\text{solute}) = 14.76 \text{ g of Ca(NO}_3)_2 \quad (2.70)$$

Solution to Exercise 2.3.1 (p. 132)

$$M_w = \frac{(9 \text{ mol} \times (30,000 \text{ g/mol})^2) + (5 \text{ mol} \times (50,000 \text{ g/mol})^2)}{(9 \text{ mol} \times 30,000 \text{ g/mol}) + (5 \text{ mol} \times 50,000 \text{ g/mol})} = 40,000 \text{ g/mol}$$

Solution to Exercise 2.3.2 (p. 132)

$$M_z = \frac{(10 \text{ mol} \times (20,000 \text{ g/mol})^3) + (2 \text{ mol} \times (50,000 \text{ g/mol})^3)}{(10 \text{ mol} \times (20,000 \text{ g/mol})^2) + (2 \text{ mol} \times (50,000 \text{ g/mol})^2)} = 100,000 \text{ g/mol}$$

Chapter 3

Chemical Speciation

3.1 Magnetism

3.1.1 Magnetism¹

3.1.1.1 Magnetic moments

The magnetic moment of a material is the incomplete cancellation of the atomic magnetic moments in that material. Electron spin and orbital motion both have magnetic moments associated with them (Figure 3.1), but in most atoms the electronic moments are oriented usually randomly so that overall in the material they cancel each other out (Figure 3.2), this is called diamagnetism.

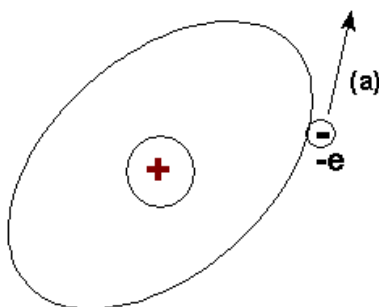


Figure 3.1: Orbital magnetic moment.

¹This content is available online at <<http://cnx.org/content/m22749/1.4/>>.

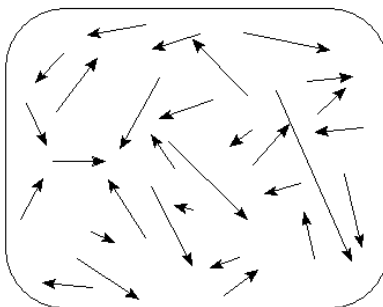


Figure 3.2: Magnetic moments in a diamagnetic sample.

If the cancellation of the moments is incomplete then the atom has a net magnetic moment. There are many subclasses of magnetic ordering such as para-, superpara-, ferro-, antiferro- or ferrimagnetism which can be displayed in a material and which usually depends, upon the strength and type of magnetic interactions and external parameters such as temperature and crystal structure atomic content and the magnetic environment which a material is placed in.

$$\mu_B = \frac{eh}{4\pi m} = 9.72 \times 10^{-24} \text{ J/T}$$

The magnetic moments of atoms, molecules or formula units are often quoted in terms of the Bohr magneton, which is equal to the magnetic moment due to electron spin

3.1.1.2 Magnetization

The magnetism of a material, the extent to which a material is magnetic, is not a static quantity, but varies compared to the environment that a material is placed in. It is similar to the temperature of a material. For example if a material is placed in an oven it will heat up to a temperature similar to that of the oven. However the speed of heating of that material, and also that of cooling are determined by the atomic structure of the material. The magnetization of a material is similar. When a material is placed in a magnetic field it may become magnetized to an extent and retain that magnetization after it is removed from the field. The extent of magnetization, and type of magnetization and the length of time that a material remains magnetized, depends again on the atomic makeup of the material.

Measuring a material's magnetism can be done on a micro or macro scale. Magnetism is measured over two parameters direction and strength. Thus magnetization has a vector quantity. The simplest form of a magnetometer is a compass. It measures the direction of a magnetic field. However more sophisticated instruments have been developed which give a greater insight into a material's magnetism.

So what exactly are you reading when you observe the output from a magnetometer?

The magnetism of a sample is called the magnetic moment of that sample and will be called that from now on. The single value of magnetic moment for the sample, is a combination of the magnetic moments on the atoms within the sample (Figure 3.3), it is also the type and level of magnetic ordering and the physical dimensions of the sample itself.

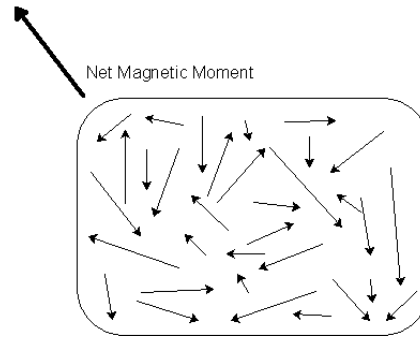


Figure 3.3: Schematic representations of the net magnetic moment in a diamagnetic sample.

The "intensity of magnetization", M , is a measure of the magnetization of a body. It is defined as the magnetic moment per unit volume or

$$M = m/V$$

with units of Am (emucm³ in cgs notation).

A material contains many atoms and their arrangement affects the magnetization of that material. In Figure 3.4 (a) a magnetic moment m is contained in unit volume. This has a magnetization of m Am. Figure 3.4 (b) shows two such units, with the moments aligned parallel. The vector sum of moments is $2m$ in this case, but as the both the moment and volume are doubled M remains the same. In Figure 3.4 (c) the moments are aligned antiparallel. The vector sum of moments is now 0 and hence the magnetization is 0 Am.

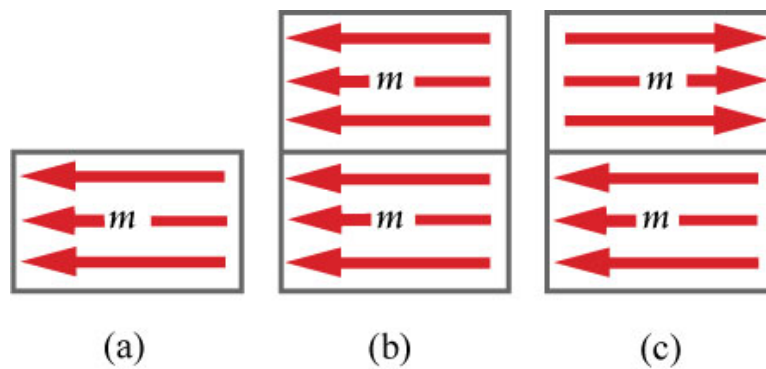


Figure 3.4: Effect of moment alignment on magnetization: (a) Single magnetic moment, (b) two identical moments aligned parallel and (c) antiparallel to each other. Adapted from J. Bland Thesis M. Phys (Hons)., 'A Mossbauer spectroscopy and magnetometry study of magnetic multilayers and oxides.' Oliver Lodge Labs, Dept. Physics, University of Liverpool

Scenarios (b) and (c) are a simple representation of ferro- and antiferromagnetic ordering. Hence we would expect a large magnetization in a ferromagnetic material such as pure iron and a small magnetization

in an antiferromagnet such as $\gamma\text{-Fe}_2\text{O}_3$

3.1.1.3 Magnetic Response

When a material is passed through a magnetic field it is affected in two ways:

1. Through its susceptibility.
2. Through its permeability.

3.1.1.3.1 Magnetic susceptibility

The concept of magnetic moment is the starting point when discussing the behavior of magnetic materials within a field. If you place a bar magnet in a field it will experience a torque or *moment* tending to align its axis in the direction of the field. A compass needle behaves in the same way. This torque increases with the strength of the poles and their distance apart. So the value of magnetic moment tells you, in effect, 'how big a magnet' you have.

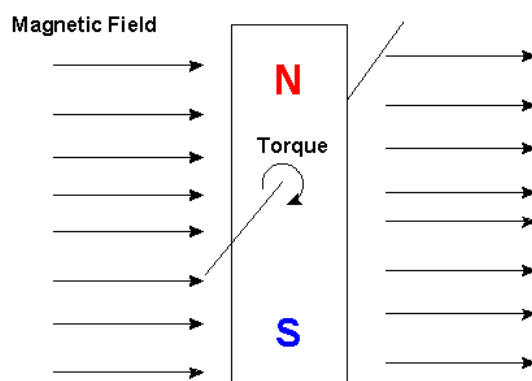


Figure 3.5: Schematic representation of the torque or moment that a magnet experiences when it is placed in a magnetic field. The magnetic will try to align with the magnetic field.

If you place a material in a weak magnetic field, the magnetic field may not overcome the binding energies that keep the material in a non magnetic state. This is because it is energetically more favorable for the material to stay exactly the same. However, if the strength of the magnetic moment is increased, the torque acting on the smaller moments in the material, it may become energetically more preferable for the material to become magnetic. The reasons that the material becomes magnetic depends on factors such as crystal structure the temperature of the material and the strength of the field that it is in. However a simple explanation of this is that as the magnetic moment strength increases it becomes more favorable for the small fields to align themselves along the path of the magnetic field, instead of being opposed to the system. For this to occur the material must rearrange its magnetic makeup at the atomic level to lower the energy of the system and restore a balance.

It is important to remember that when we consider the magnetic susceptibility and take into account how a material changes on the atomic level when it is placed in a magnetic field with a certain moment. The moment that we are measuring with our magnetometer is the total moment of that sample.

$$\chi = \frac{M}{H}$$

where χ = susceptibility, M = variation of magnetization, and H = applied field.

3.1.1.3.2 Magnetic permeability

Magnetic permeability is the ability of a material to conduct an electric field. In the same way that materials conduct or resist electricity, materials also conduct or resist a magnetic flux or the flow of magnetic lines of force (Figure 3.6).

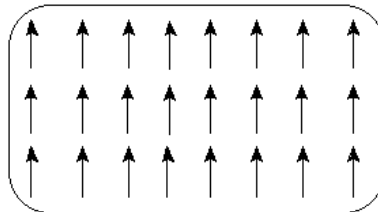


Figure 3.6: Magnetic ordering in a ferromagnetic material.

Ferromagnetic materials are usually highly permeable to magnetic fields. Just as electrical conductivity is defined as the ratio of the current density to the electric field strength, so the magnetic permeability, μ , of a particular material is defined as the ratio of flux density to magnetic field strength. However unlike in electrical conductivity magnetic permeability is nonlinear.

$$\mu = B/H$$

Permeability, where μ is written without a subscript, is known as absolute permeability. Instead a variant is used called relative permeability.

$$\mu = \mu_0 \times \mu_r$$

Absolute permeability is a variation upon 'straight' or absolute permeability, μ , but is more useful as it makes clearer how the presence of a particular material affects the relationship between flux density and field strength. The term 'relative' arises because this permeability is defined in relation to the permeability of a vacuum, μ_0 .

$$\mu_r = \mu/\mu_0$$

For example, if you use a material for which $\mu_r = 3$ then you know that the flux density will be three times as great as it would be if we just applied the same field strength to a vacuum.

3.1.1.3.2.1 Initial permeability

Initial permeability describes the relative permeability of a material at low values of B (below 0.1 T). The maximum value for μ in a material is frequently a factor of between 2 and 5 or more above its initial value.

Low flux has the advantage that every ferrite can be measured at that density without risk of saturation. This consistency means that comparison between different ferrites is easy. Also, if you measure the inductance with a normal component bridge then you are doing so with respect to the initial permeability.

3.1.1.3.2 Permeability of a vacuum in the SI

The permeability of a vacuum has a finite value - about $1.257 \times 10^{-6} \text{ H m}^{-1}$ - and is denoted by the symbol μ_0 . Note that this value is constant with field strength and temperature. Contrast this with the situation in ferromagnetic materials where μ is strongly dependent upon both. Also, for practical purposes, most non-ferromagnetic substances (such as wood, plastic, glass, bone, copper aluminum, air and water) have permeability almost equal to μ_0 ; that is, their relative permeability is 1.0.

The permeability, μ , the variation of magnetic induction,

$$B = \mu_o(H + M)$$

with applied field,

$$\mu = B/H$$

3.1.1.4 Background contributions

A single measurement of a sample's magnetization is relatively easy to obtain, especially with modern technology. Often it is simply a case of loading the sample into the magnetometer in the correct manner and performing a single measurement. This value is, however, the sum total of the sample, any substrate or backing and the sample mount. A sample substrate can produce a substantial contribution to the sample total.

For substrates that are diamagnetic, under zero applied field, this means it has no effect on the measurement of magnetization. Under applied fields its contribution is linear and temperature independent. The diamagnetic contribution can be calculated from knowledge of the volume and properties of the substrate and subtracted as a constant linear term to produce the signal from the sample alone. The diamagnetic background can also be seen clearly at high fields where the sample has reached saturation: the sample saturates but the linear background from the substrate continues to increase with field. The gradient of this background can be recorded and subtracted from the readings if the substrate properties are not known accurately.

3.1.1.5 Hysteresis

When a material exhibits hysteresis, it means that the material responds to a force and has a history of that force contained within it. Consider if you press on something until it depresses. When you release that pressure, if the material remains depressed and doesn't spring back then it is said to exhibit some type of hysteresis. It remembers a history of what happened to it, and may exhibit that history in some way. Consider a piece of iron that is brought into a magnetic field, it retains some magnetization, even after the external magnetic field is removed. Once magnetized, the iron will stay magnetized indefinitely. To demagnetize the iron, it is necessary to apply a magnetic field in the opposite direction. This is the basis of memory in a hard disk drive.

The response of a material to an applied field and its magnetic hysteresis is an essential tool of magnetometry. Paramagnetic and diamagnetic materials can easily be recognized, soft and hard ferromagnetic materials give different types of hysteresis curves and from these curves values such as saturation magnetization, remnant magnetization and coercivity are readily observed. More detailed curves can give indications of the type of magnetic interactions within the sample.

3.1.1.6 Diamagnetism and paramagnetism

The intensity of magnetization depends upon both the magnetic moments in the sample and the way that they are oriented with respect to each other, known as the magnetic ordering.

Diamagnetic materials, which have no atomic magnetic moments, have no magnetization in zero field. When a field is applied a small, negative moment is induced on the diamagnetic atoms proportional to the applied field strength. As the field is reduced the induced moment is reduced.

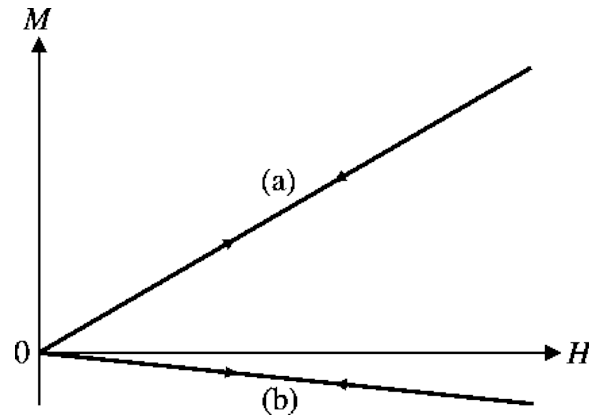


Figure 3.7: Typical effect on the magnetization, M , of an applied magnetic field, H , on (a) a paramagnetic system and (b) a diamagnetic system. Adapted from J. Bland Thesis M. Phys (Hons)., 'A Mossbauer spectroscopy and magnetometry study of magnetic multilayers and oxides.' Oliver Lodge Labs, Dept. Physics, University of Liverpool

In a paramagnet the atoms have a net magnetic moment but are oriented randomly throughout the sample due to thermal agitation, giving zero magnetization. As a field is applied the moments tend towards alignment along the field, giving a net magnetization which increases with applied field as the moments become more ordered. As the field is reduced the moments become disordered again by their thermal agitation. The figure shows the linear response $M \propto H$ where $\mu H \ll kT$.

3.1.1.7 Ferromagnetism

The hysteresis curves for a ferromagnetic material are more complex than those for diamagnets or paramagnets. Below diagram shows the main features of such a curve for a simple ferromagnet.

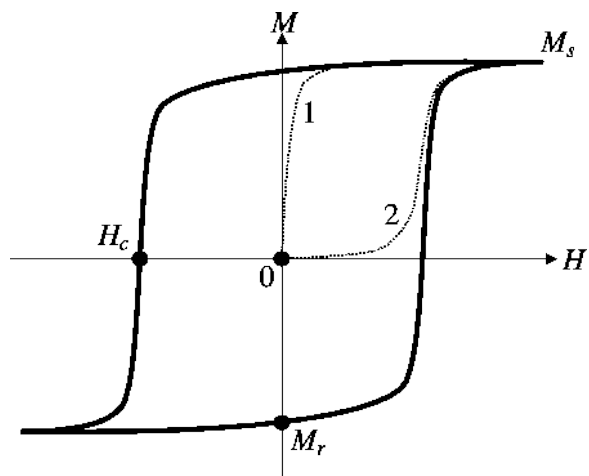


Figure 3.8: Schematic of a magnetization hysteresis loop in a ferromagnetic material showing the saturation magnetization, M_s , coercive field, H_c , and remnant magnetization, M_r . Virgin curves are shown dashed for nucleation (1) and pinning (2) type magnets. Adapted from J. Bland Thesis M. Phys (Hons)., 'A Mossbauer spectroscopy and magnetometry study of magnetic multilayers and oxides.' Oliver Lodge Labs, Dept. Physics, University of Liverpool

In the virgin material (point 0) there is no magnetization. The process of magnetization, leading from point 0 to saturation at $M = M_s$, is outlined below. Although the material is ordered ferromagnetically it consists of a number of ordered domains arranged randomly giving no net magnetization. This is shown in below (a) with two domains whose individual saturation moments, M_s , lie antiparallel to each other.

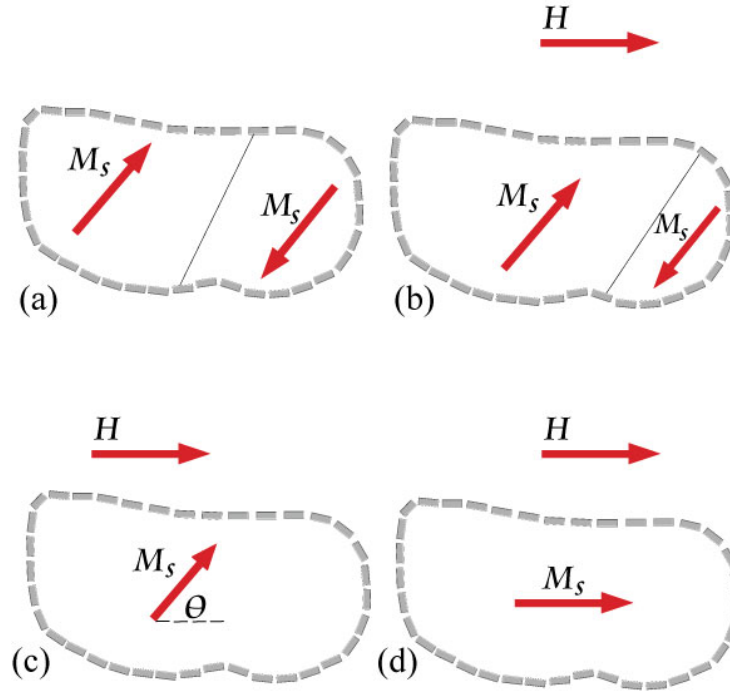


Figure 3.9: The process of magnetization in a demagnetized ferromagnet. Adapted from J. Bland Thesis M. Phys (Hons)., 'A Mossbauer spectroscopy and magnetometry study of magnetic multilayers and oxides.' Oliver Lodge Labs, Dept. Physics, University of Liverpool

As the magnetic field, H , is applied, (b), those domains which are more energetically favorable increase in size at the expense of those whose moment lies more antiparallel to H . There is now a net magnetization; M . Eventually a field is reached where all of the material is a single domain with a moment aligned parallel, or close to parallel, with H . The magnetization is now $M = M_s \cos \theta$ where θ is the angle between M_s along the easy magnetic axis and H . Finally M_s is rotated parallel to H and the ferromagnet is saturated with a magnetization $M = M_s$.

The process of domain wall motion affects the shape of the virgin curve. There are two qualitatively different modes of behavior known as nucleation and pinning, shown in Figure 3.8 as curves 1 and 2, respectively.

In a nucleation-type magnet saturation is reached quickly at a field much lower than the coercive field. This shows that the domain walls are easily moved and are not pinned significantly. Once the domain structure has been removed the formation of reversed domains becomes difficult, giving high coercivity. In a pinning-type magnet fields close to the coercive field are necessary to reach saturation magnetization. Here the domain walls are substantially pinned and this mechanism also gives high coercivity.

3.1.1.8 Remnance

As the applied field is reduced to 0 after the sample has reached saturation the sample can still possess a remnant magnetization, M_r . The magnitude of this remnant magnetization is a product of the saturation magnetization, the number and orientation of easy axes and the type of anisotropy symmetry. If the axis of anisotropy or magnetic easy axis is perfectly aligned with the field then $M_r = M_s$, and if perpendicular

$M_r = 0$.

At saturation the angular distribution of domain magnetizations is closely aligned to H . As the field is removed they turn to the nearest easy magnetic axis. In a cubic crystal with a positive anisotropy constant, K_1 , the easy directions are $\langle 100 \rangle$. At remnance the domain magnetizations will lie along one of the three $\langle 100 \rangle$ directions. The maximum deviation from H occurs when H is along the $\langle 111 \rangle$ axis, giving a cone of distribution of 55° around the axis. Averaging the saturation magnetization over this angle gives a remnant magnetization of $0.832 M_s$.

3.1.1.9 Coercivity

The coercive field, H_c , is the field at which the remnant magnetization is reduced to zero. This can vary from a few Am for soft magnets to 10^7 Am for hard magnets. It is the point of magnetization reversal in the sample, where the barrier between the two states of magnetization is reduced to zero by the applied field allowing the system to make a Barkhausen jump to a lower energy. It is a general indicator of the energy gradients in the sample which oppose large changes of magnetization.

The reversal of magnetization can come about as a rotation of the magnetization in a large volume or through the movement of domain walls under the pressure of the applied field. In general materials with few or no domains have a high coercivity whilst those with many domains have a low coercivity. However, domain wall pinning by physical defects such as vacancies, dislocations and grain boundaries can increase the coercivity.

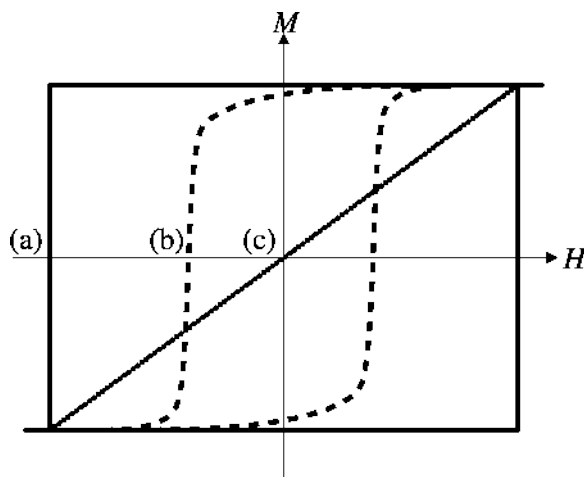


Figure 3.10: Shape of hysteresis loop as a function of Θ_H , the angle between anisotropy axis and applied field H , for: (a) $\Theta_H = 0^\circ$, (b) 45° and (c) 90° . Adapted from J. Bland Thesis M. Phys (Hons)., 'A Mossbauer spectroscopy and magnetometry study of magnetic multilayers and oxides.' Oliver Lodge Labs, Dept. Physics, University of Liverpool

The loop illustrated in Figure 3.10 is indicative of a simple bi-stable system. There are two energy minima: one with magnetization in the positive direction, and another in the negative direction. The depth of these minima is influenced by the material and its geometry and is a further parameter in the strength of the coercive field. Another is the angle, Θ_H , between the anisotropy axis and the applied field. The above fig shows how the shape of the hysteresis loop and the magnitude of H_c varies with Θ_H . This effect shows the importance of how samples with strong anisotropy are mounted in a magnetometer when comparing loops.

3.1.1.10 Temperature dependence

A hysteresis curve gives information about a magnetic system by varying the applied field but important information can also be gleaned by varying the temperature. As well as indicating transition temperatures, all of the main groups of magnetic ordering have characteristic temperature/magnetization curves. These are summarized in Figure 3.11 and Figure 3.12. At all temperatures a diamagnet displays only any magnetization induced by the applied field and a small, negative susceptibility.

The curve shown for a paramagnet (Figure 3.11) is for one obeying the Curie law,

$$\chi = \frac{C}{T}$$

and so intercepts the axis at $T = 0$. This is a subset of the Curie-Weiss law,

$$\chi = \frac{C}{T - \theta}$$

where θ is a specific temperature for a particular substance (equal to 0 for paramagnets).

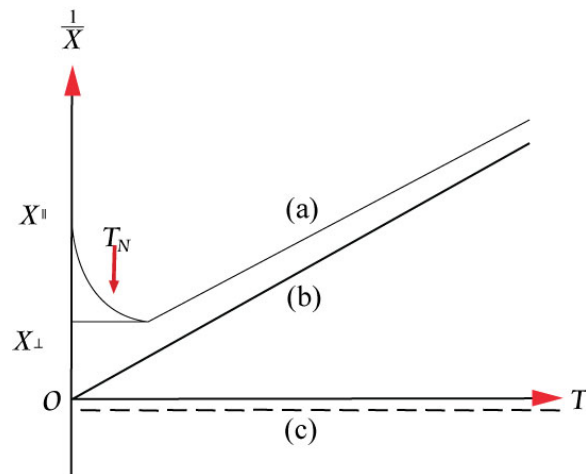


Figure 3.11: Variation of reciprocal susceptibility with temperature for: (a) antiferromagnetic, (b) paramagnetic and (c) diamagnetic ordering. Adapted from J. Bland Thesis M. Phys (Hons), 'A Mossbauer spectroscopy and magnetometry study of magnetic multilayers and oxides.' Oliver Lodge Labs, Dept. Physics, University of Liverpool

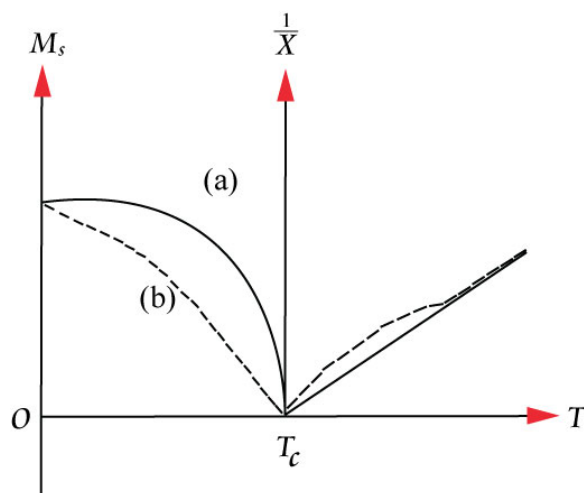


Figure 3.12: Variation of saturation magnetization below, and reciprocal susceptibility above T_c for: (a) ferromagnetic and (b) ferrimagnetic ordering. Adapted from J. Bland Thesis M. Phys (Hons)., 'A Mossbauer spectroscopy and magnetometry study of magnetic multilayers and oxides.' Oliver Lodge Labs, Dept. Physics, University of Liverpool

Above T_N and T_C both antiferromagnets and ferromagnets behave as paramagnets with $1/\chi$ linearly proportional to temperature. They can be distinguished by their intercept on the temperature axis, $T = \Theta$. Ferromagnetics have a large, positive Θ , indicative of their strong interactions. For paramagnetics $\Theta = 0$ and antiferromagnetics have a negative Θ .

The net magnetic moment per atom can be calculated from the gradient of the straight line graph of $1/\chi$ versus temperature for a paramagnetic ion, rearranging Curie's law to give

$$\mu = \sqrt{\frac{3Ak}{N_x}}$$

where A is the atomic mass, k is Boltzmann's constant, N is the number of atoms per unit volume and x is the gradient.

Ferromagnets below T_C display spontaneous magnetization. Their susceptibility above T_C in the paramagnetic region is given by the Curie-Weiss law

where g is the gyromagnetic constant. In the ferromagnetic phase with T greater than T_C the magnetization $M(T)$ can be simplified to a power law, for example the magnetization as a function of temperature can be given by

$$M(T) \approx (T_c - T)^\beta$$

where the term β is typically in the region of 0.33 for magnetic ordering in three dimensions.

The susceptibility of an antiferromagnet increases to a maximum at T_N as temperature is reduced, then decreases again below T_N . In the presence of crystal anisotropy in the system this change in susceptibility depends on the orientation of the spin axes: χ (parallel) decreases with temperature whilst χ (perpendicular) is constant. These can be expressed as

$$\chi_{\perp} = \frac{C}{2\theta}$$

where C is the Curie constant and Θ is the total change in angle of the two sublattice magnetizations away from the spin axis, and

$$\chi \parallel = \frac{2n_g\mu_H^2 B'(J, a'_0)}{2kT + n_g\mu_H^2 \gamma \rho B'(J, a'_0)}$$

where n_g is the number of magnetic atoms per gramme, B' is the derivative of the Brillouin function with respect to its argument a' , evaluated at a'_0 , μ_H is the magnetic moment per atom and γ is the molecular field coefficient.

3.1.1.11 Bibliography

- U. Gradmann, Handbook of Magnetic Materials, vol. 7.
- B. D. Cullity, *Introduction to Magnetic Materials*, Addison-Wesley, Massachusettes (1972).
- G. Bertotti, *Hysteresis in Magnetism*, Academic Press, San Diego (1998).
- S. Chikazumi, S. H. Charap, *Physics of Magnetism*, Krieger Publishing Company (1978).
- J. Bland, Thesis M. Phys (Hons)., 'A Mossbauer spectroscopy and magnetometry study of magnetic multilayers and oxides.' Oliver Lodge Labs, Dept. Physics, University of Liverpool.

3.1.2 Theory of A Superconducting Quantum Interference Device (SQUID)²

3.1.2.1 Introduction

One of the most sensitive forms of magnetometry is SQUID magnetometry. This technique uses a combination of superconducting materials and Josephson junctions to measure magnetic fields with resolutions up to $\sim 10^{-14}$ kG or greater. In the proceeding pages we will describe how a SQUID actually works.

3.1.2.2 Electron-pair waves

In superconductors the resistanceless current is carried by pairs of electrons, known as Cooper Pairs. A Cooper Pair is a pair of electrons. Each electron has a quantized wavelength. With a Cooper pair each electrons wave couples with its opposite number over a large distances. This phenomenon is a result of the very low temperatures at which many materials will superconduct.

What exactly is superconductance? When a material is at very low temperatures, its crystal lattice behaves differently than when it higher temperatures. Usually at higher temperatures a material will have large vibrations called in the crystal lattice. These vibrations scatter electrons as they pass through this lattice (Figure 3.13), and this is the basis for bad conductance.

²This content is available online at <<http://cnx.org/content/m22750/1.3/>>.

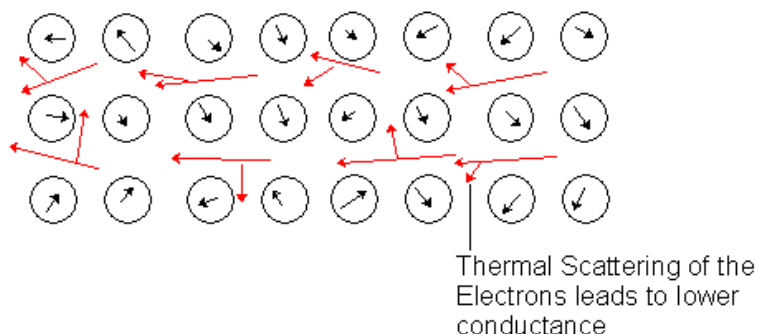


Figure 3.13: Schematic representation of the scattering of electrons as they pass through a vibrating lattice.

With a superconductor the material is designed to have very small vibrations, these vibrations are lessened even more by cooling the material to extremely low temperatures. With no vibrations there is no scattering of the electrons and this allows the material to superconduct.

The origin of a Cooper pair is that as the electron passes through a crystal lattice at superconducting temperatures it negative charge pulls on the positive charge of the nuclei in the lattice through coulombic interactions producing a ripple. An electron traveling in the opposite direction is attracted by this ripple. This is the origin of the coupling in a Cooper pair (Figure 3.14).

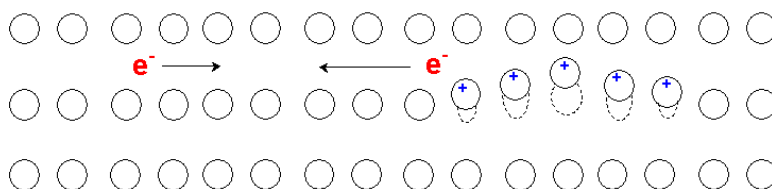


Figure 3.14: Schematic representation of the Cooper pair coupling model.

A passing electron attracts the lattice, causing a slight ripple toward its path. Another electron passing in the opposite direction is attracted to that displacement (Figure 3.15).

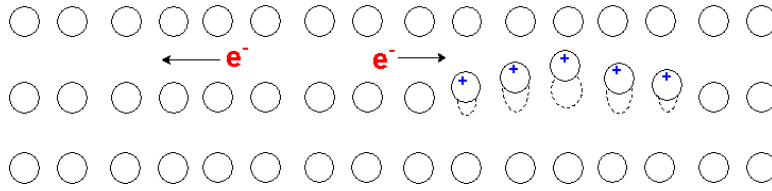


Figure 3.15: Schematic representation of Cooper pair coupling

Due to the coupling and the fact that for each pair there is two spin states (Figure 3.16).

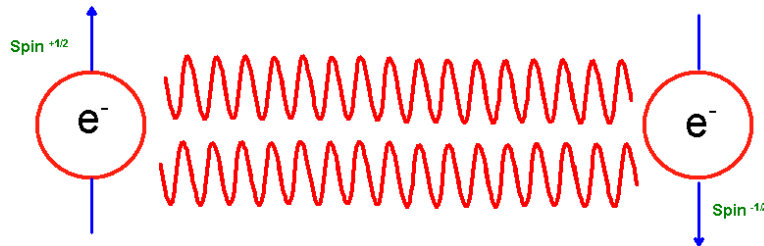


Figure 3.16: Schematic representation of the condensation of the wavelengths of a Cooper pairs

Each pair can be treated as a single particle with a whole spin, not half a spin such as is usually the case with electrons. This is important, as an electron which is classed in a group of matter called Fermions are governed by the Fermi exclusion principle which states that anything with a spin of one half cannot occupy the same space as something with the same spin of one half. This turns the electron means that a Cooper pair is in fact a Boson the opposite of a Fermion and this allows the Coopers pairs to condensate into one wave packet. Each Coopers pair has a mass and charge twice that of a single electron, whose velocity is that of the center of mass of the pair. This coupling can only happen in extremely cold conditions as thermal vibrations become greater than the force that an electron can exert on a lattice. And thus scattering occurs.

Each pair can be represented by a wavefunction of the form

$$\Phi_P = \Phi e^{i(P \cdot r)/\hbar}$$

where P is the net momentum of the pair whose center of mass is at r . However, all the Cooper pairs in a superconductor can be described by a single wavefunction yet again due to the fact that the electrons are in a Coopers pair state and are thus Bosons in the absence of a current because all the pairs have the same phase - they are said to be "phase coherent"

$$\Psi_P = \Psi e^{i(P \cdot r)/\hbar}$$

This electron-pair wave retains its phase coherence over long distances, and essentially produces a standing wave over the device circuit. In a SQUID there are two paths which form a circle and are made with the same standing wave (Figure 3.17). The wave is split in two sent off along different paths, and then recombined to record an interference pattern by adding the difference between the two.

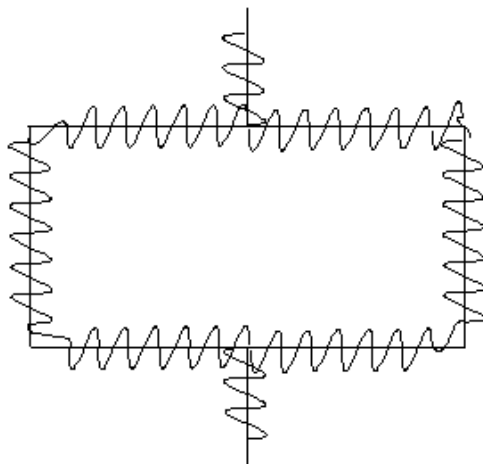


Figure 3.17: Schematic representation of a standing wave across a SQUID circuit.

This allows measurement at any phase differences between the two components, which if there is no interference will be exactly the same, but if there is a difference in their path lengths or in some interaction that the waves encounters such as a magnetic field it will correspond in a phase difference at the end of each path length.

A good example to use is of two water waves emanating from the same point. They will stay in phase if they travel the same distance, but will fall out of phase if one of them has to deviate around an obstruction such as a rock. Measuring the phase difference between the two waves then provides information about the obstruction.

3.1.2.3 Phase and coherence

Another implication of this long range coherence is the ability to calculate phase and amplitude at any point on the wave's path from the knowledge of its phase and amplitude at any single point, combined with its wavelength and frequency. The wavefunction of the electron-pair wave in the above eqn. can be rewritten in the form of a one-dimensional wave as

$$\Psi_p = \Psi \sin 2\pi \left(\frac{x}{\lambda} - vt \right)$$

If we take the wave frequency, V , as being related to the kinetic energy of the Cooper pair with a wavelength, λ , being related to the momentum of the pair by the relation $\lambda = h/p$ then it is possible to evaluate the phase difference between two points in a current carrying superconductor.

If a resistanceless current flows between points X and Y on a superconductor there will be a phase difference between these points that is constant in time.

3.1.2.4 Effect of a magnetic field

The parameters of a standing wave are dependent on a current passing through the circuit; they are also strongly affected by an applied magnetic field. In the presence of a magnetic field the momentum, p , of a particle with charge q in the presence of a magnetic field becomes $mV + qA$ where A is the magnetic vector potential. For electron-pairs in an applied field their moment P is now equal to $2mV + 2eA$.

In an applied magnetic field the phase difference between points X and Y is now a combination of that due to the supercurrent and that due to the applied field.

3.1.2.5 The fluxoid

One effect of the long range phase coherence is the quantization of magnetic flux in a superconducting ring. This can either be a ring, or a superconductor surrounding a non-superconducting region. Such an arrangement can be seen in Figure 3.18 where region N has a flux density B within it due to supercurrents flowing around it in the superconducting region S.

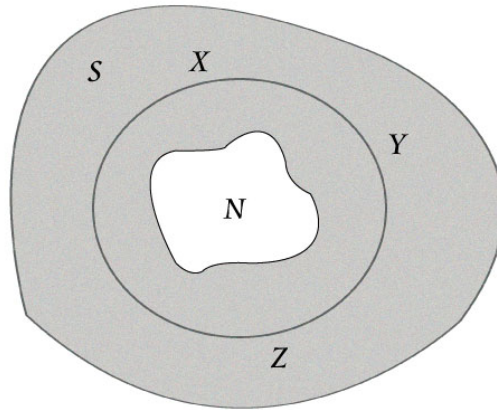


Figure 3.18: Superconductor enclosing a non-superconducting region. Adapted from J. Bland Thesis M. Phys (Hons)., 'A Mossbauer spectroscopy and magnetometry study of magnetic multilayers and oxides.' Oliver Lodge Labs, Dept. Physics, University of Liverpool.

In the closed path XYZ encircling the non-superconducting region there will be a phase difference of the electron-pair wave between any two points, such as X and Y, on the curve due to the field and the circulating current.

If the superelectrons are represented by a single wave then at any point on XYZX it can only have one value of phase and amplitude. Due to the long range coherence the phase is single valued also called quantized meaning around the circumference of the ring $\Delta\phi$ must equal $2\pi n$ where n is any integer. Due to the wave only having a single value the fluxoid can only exist in quantized units. This quantum is termed the fluxon, ϕ_0 , given by

$$\Phi_0 = \frac{h}{2e} = 2.07 \times 10^{-15} \text{ Wb}$$

3.1.2.6 Josephson tunneling

If two superconducting regions are kept totally isolated from each other the phases of the electron-pairs in the two regions will be unrelated. If the two regions are brought together then as they come close electron-pairs will be able to tunnel across the gap and the two electron-pair waves will become coupled. As the separation

decreases, the strength of the coupling increases. The tunneling of the electron-pairs across the gap carries with it a superconducting current as predicted by B.D. Josephson and is called "Josephson tunneling" with the junction between the two superconductors called a "Josephson junction" (Figure 3.19).

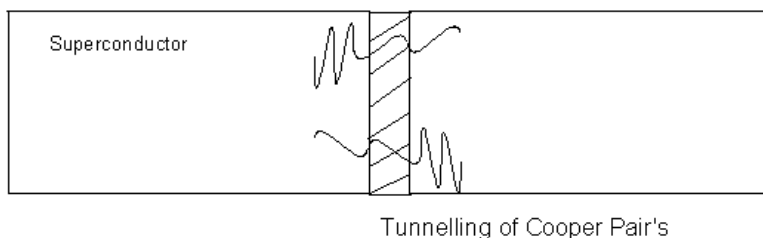


Figure 3.19: Schematic representation of the tunneling of Cooper pairs across a Josephson junction.

The Josephson tunneling junction is a special case of a more general type of weak link between two superconductors. Other forms include constrictions and point contacts but the general form is of a region between two superconductors which has a much lower critical current and through which a magnetic field can penetrate.

3.1.2.7 Superconducting quantum interference device (SQUID)

A superconducting quantum interference device (SQUID) uses the properties of electron-pair wave coherence and Josephson Junctions to detect very small magnetic fields. The central element of a SQUID is a ring of superconducting material with one or more weak links called Josephesons Junctions. An example is shown in the below. With weak-links at points W and X whose critical current, i_c , is much less than the critical current of the main ring. This produces a very low current density making the momentum of the electron-pairs small. The wavelength of the electron-pairs is thus very long leading to little difference in phase between any parts of the ring.

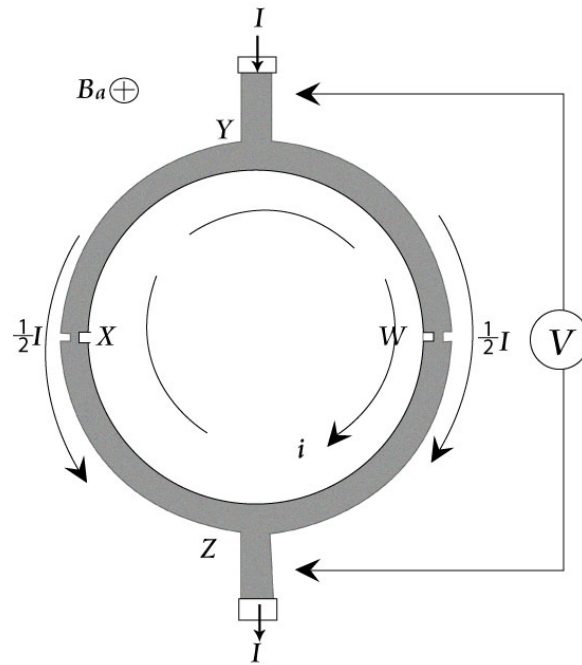


Figure 3.20: Superconducting quantum interference device (SQUID) as a simple magnetometer. Adapted from J. Bland Thesis M. Phys (Hons)., 'A Mossbauer spectroscopy and magnetometry study of magnetic multilayers and oxides.' Oliver Lodge Labs, Dept. Physics, University of Liverpool.

If a magnetic field, B_a , is applied perpendicular to the plane of the ring (Figure 3.21), a phase difference is produced in the electron-pair wave along the path XYW and WZX . One of the features of a superconducting loop is that the magnetic flux, Φ , passing through it which is the product of the magnetic field and the area of the loop and is quantized in units of $\Phi_0 = h / (2e)$, where h is Planck's constant, $2e$ is the charge of the Cooper pair of electrons, and Φ_0 has a value of 2×10^{-15} tesla m^2 . If there are no obstacles in the loop, then the superconducting current will compensate for the presence of an arbitrary magnetic field so that the total flux through the loop (due to the external field plus the field generated by the current) is a multiple of Φ_0 .

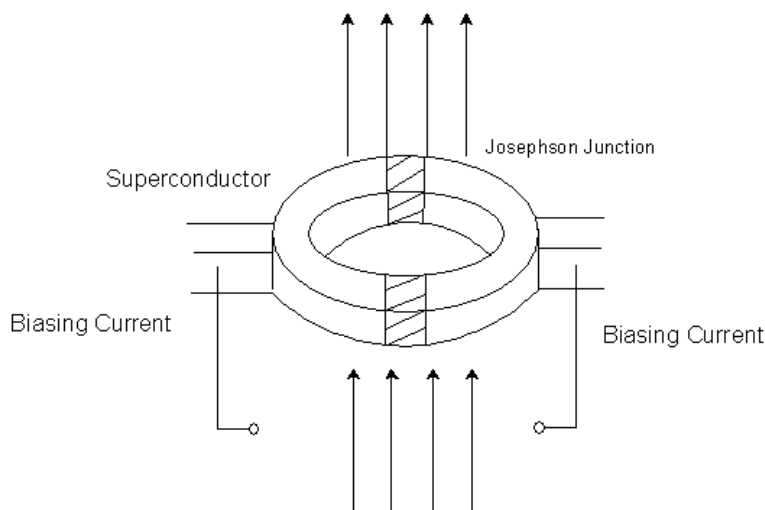


Figure 3.21: Schematic representation of a SQUID placed in a magnetic field.

Josephson predicted that a superconducting current can be sustained in the loop, even if its path is interrupted by an insulating barrier or a normal metal. The SQUID has two such barriers or 'Josephson junctions'. Both junctions introduce the same phase difference when the magnetic flux through the loop is 0 , Φ_0 , $2\Phi_0$ and so on, which results in constructive interference, and they introduce opposite phase difference when the flux is $\Phi_0/2$, $3\Phi_0/2$ and so on, which leads to destructive interference. This interference causes the critical current density, which is the maximum current that the device can carry without dissipation, to vary. The critical current is so sensitive to the magnetic flux through the superconducting loop that even tiny magnetic moments can be measured. The critical current is usually obtained by measuring the voltage drop across the junction as a function of the total current through the device. Commercial SQUIDS transform the modulation in the critical current to a voltage modulation, which is much easier to measure.

An applied magnetic field produces a phase change around a ring, which in this case is equal

$$\Delta\phi(B) = 2\pi \frac{\Phi_a}{\Phi_0}$$

where Φ_a is the flux produced in the ring by the applied magnetic field. The magnitude of the critical measuring current is dependent upon the critical current of the weak-links and the limit of the phase change around the ring being an integral multiple of 2π . For the whole ring to be superconducting the following condition must be met

$$\alpha + \beta + 2\pi \frac{\Phi_a}{\Phi_0} = n \cdot 2\pi$$

where α and β are the phase changes produced by currents across the weak-links and $2\pi\Phi_a/\Phi_0$ is the phase change due to the applied magnetic field.

When the measuring current is applied α and β are no longer equal, although their sum must remain constant. The phase changes can be written as

$$\alpha = \pi \left[n - \frac{\Phi_a}{\Phi_o} \right] - \delta$$

$$\beta = \pi \left[n - \frac{\Phi_a}{\Phi_o} \right] + \delta$$

where δ is related to the measuring current I . Using the relation between current and phase from the above Eqn. and rearranging to eliminate i we obtain an expression for I ,

$$I_c = 2i_c \left| \cos \pi \frac{\Phi_a}{\Phi_o} \cdot \sin \delta \right|$$

As $\sin \delta$ cannot be greater than unity we can obtain the critical measuring current, I_c from the above

$$I_c = 2i_c \left| \cos \pi \frac{\Phi_a}{\Phi_o} \right|$$

which gives a periodic dependence on the magnitude of the magnetic field, with a maximum when this field is an integer number of fluxons and a minimum at half integer values as shown in the below figure.

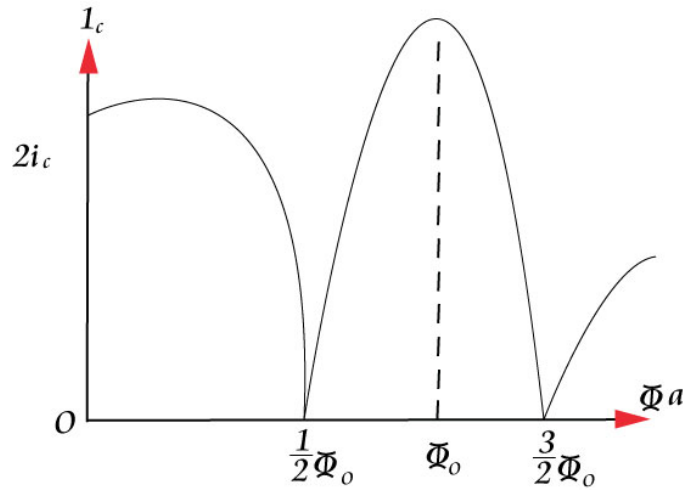


Figure 3.22: Critical measuring current, I_c , as a function of applied magnetic field. Adaped from J. Bland Thesis M. Phys (Hons)., 'A Mossbauer spectroscopy and magnetometry study of magnetic multilayers and oxides.' Oliver Lodge Labs, Dept. Physics, University of Liverpool.

3.1.2.8 Bibliography

- J. Bland, Thesis M. Phys (Hons)., 'A Mossbauer spectroscopy and magnetometry study of magnetic multilayers and oxides.' Oliver Lodge Labs, Dept. Physics, University of Liverpool.

- J. P. Cleuziou, W. Wernsdorfer, V. Bouchiat, T. Ondarçuhu, and M. Monthieux, *Nature Nanotech.*, 2006, **1**, 53.
- W. G. Jenksy, S. S. H. Sadeghiz, and J. P. Wikswo Jr., *J. Phys. D: Appl. Phys.*, 1997, **30**, 293.
- R. L. Fagaly, *Review of Scientific Instruments*, 2006, **77**, 101101.
- Quantum Design, Operating manual for the MPMS, 1999.

3.1.3 Practical Guide to Using a Superconducting Quantum Interference Device³

SQUIDs offer the ability to measure at sensitivities unachievable by other magnetic sensing methodologies. However, their sensitivity requires proper attention to cryogenics and environmental noise. SQUIDs should only be used when no other sensor is adequate for the task. There are many exotic uses for SQUID however we are just concerned with the laboratory applications of SQUID.

In most physical and chemical laboratories a device called a MPMS (Figure 3.23) is used to measure the magnetic moment of a sample by reading the output of the SQUID detector. In a MPMS the sample moves upward through the electronic pick up coils called gradiometers. One upward movement is one whole scan. Multiple scans are used and added together to improve measurement resolution. After collecting the raw voltages, there is computation of the magnetic moments of the sample.

The MPMS measures the moment of a sample by moving it through a liquid Helium cooled, superconducting sensing coil. Many different measurements can be carried out using an MPMS however we will discuss just a few.



Figure 3.23: A MPMS work station.

³This content is available online at <<http://cnx.org/content/m22968/1.2/>>.

3.1.3.1 Using an magnetic property measurement dystem (MPMS)

3.1.3.1.1 DC magnetization

DC magnetization is the magnetic per unit volume (M) of a sample. If the sample doesn't have a permanent magnetic moment, a field is applied to induce one. The sample is then stepped through a superconducting detection array and the SQUID's output voltage is processed and the sample moment computed. Systems can be configured to measure hysteresis loops, relaxation times, magnetic field, and temperature dependence of the magnetic moment.

A DC field can be used to magnetize samples. Typically, the field is fixed and the sample is moved into the detection coil's region of sensitivity. The change in detected magnetization is directly proportional to the magnetic moment of the sample. Commonly referred to as SQUID magnetometers, these systems are properly called SQUID susceptometers (Figure 3.24). They have a homogeneous superconducting magnet to create a very uniform field over the entire sample measuring region and the superconducting pickup loops. The magnet induces a moment allowing a measurement of magnetic susceptibility. The superconducting detection loop array is rigidly mounted in the center of the magnet. This array is configured as a gradient coil to reject external noise sources. The detection coil geometry determines what mathematical algorithm is used to calculate the net magnetization.

An important feature of SQUIDs is that the induced current is independent of the *rate* of flux change. This provides uniform response at all frequencies i.e., true dc response and allows the sample to be moved slowly without degrading performance. As the sample passes through a coil, it changes the flux in that coil by an amount proportional to the magnetic moment M of the sample. The peak-to-peak signal from a complete cycle is thus proportional to twice M . The SQUID sensor shielded inside a niobium can is located where the fringe fields generated by the magnet are less than 10 mT. The detection coil circuitry is typically constructed using NbTi (Figure 3.25). This allows measurements in applied fields of 9 T while maintaining sensitivities of 10–8 emu. Thermal insulation not shown is placed between the detection coils and the sample tube to allow the sample temperature to be varied.

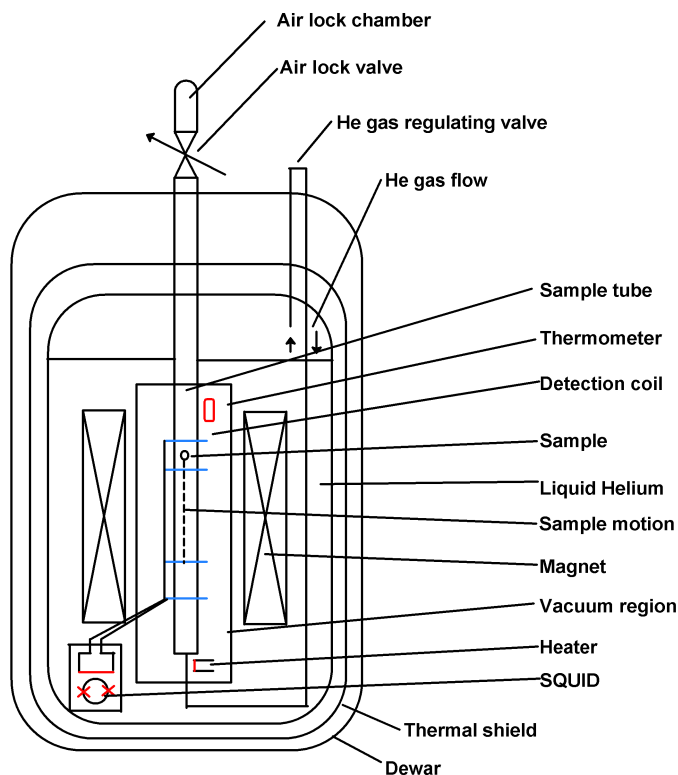


Figure 3.24: Schematic diagram of a MPMSR. Adapted from L. Fagaly, *Review of Scientific Instruments*, 2006, **77**, 101101.

The use of a variable temperature insert can allow measurements to be made over a wide range 1.8–400 K. Typically, the sample temperature is controlled by helium gas flowing slowly past the sample. The temperature of this gas is regulated using a heater located below the sample measuring region and a thermometer located above the sample region. This arrangement ensures that the entire region has reached thermal equilibrium prior to data acquisition. The helium gas is obtained from normal evaporation in the Dewar, and its flow rate is controlled by a precision regulating valve.

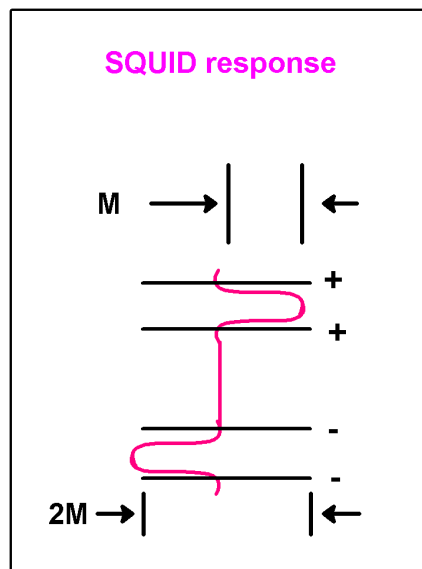


Figure 3.25: Signal output of an MPMS. Adapted from L. Fagaly, *Review of Scientific Instruments*, 2006, **77**, 101101.

3.1.3.2 Procedures when using an MPMS

3.1.3.2.1 Calibration

The magnetic moment calibration for the SQUID is determined by measuring a palladium standard over a range of magnetic fields and then by adjusting to obtain the correct moment for the standard. The palladium standard samples are effectively point sources with an accuracy of approximately 0.1%.

3.1.3.2.2 Sample mounting considerations

The type, size and geometry of a sample is usually sufficient to determine the method you use to attach it to the sample. However mostly for MPMS measurements a plastic straw is used. This is due to the straw having minimal magnetic susceptibility.

However there are a few important considerations for the sample holder design when mounting a sample for measurement in a magnetometer. The sample holder can be a major contributor to the background signal. Its contribution can be minimized by choosing materials with low magnetic susceptibility and by keeping the mass to a minimum such as a plastic straw mentioned above.

The materials used to hold a sample must perform well over the temperature range to be used. In a MPMS, the geometric arrangement of the background and sample is critical when their magnetic susceptibilities will be of similar magnitude. Thus, the sample holder should optimize the sample's positioning in the magnetometer. A sample should be mounted rigidly in order to avoid excess sample motion during measurement. A sample holder should also allow easy access for mounting the sample, and its background contribution should be easy to measure. This advisory introduces some mounting methods and discusses some of the more important considerations when mounting samples for the MPMS magnetometer. Keep in mind that these are only recommendations, not guaranteed procedures. The researcher is responsible for assuring that the methods and materials used will meet experimental requirements.

3.1.3.2.2.1 Sample Mounts

3.1.3.2.2.1.1 Platform mounting

For many types of samples, mounting to a platform is the most convenient method. The platform's mass and susceptibility should be as small as possible in order to minimize its background contribution and signal distortion.

3.1.3.2.2.1.2 Plastic disc

A plastic disc about 2 mm thick with an outside diameter equivalent to the pliable plastic tube's diameter (a clear drinking straw is suitable) is inserted and twisted into place. The platform should be fairly rigid. Mount samples onto this platform with glue. Place a second disc, with a diameter slightly less than the inside diameter of the tube and with the same mass, on top of the sample to help provide the desired symmetry. Pour powdered samples onto the platform and place a second disc on top. The powders will be able to align with the field. Make sure the sample tube is capped and ventilated.

3.1.3.2.2.1.3 Crossed threads

Make one of the lowest mass sample platforms by threading a cross of white cotton thread (colored dyes can be magnetic). Using a needle made of a nonmagnetic metal, or at least carefully cleaned, thread some white cotton sewing thread through the tube walls and tie a secure knot so that the thread platform is rigid. Glue a sample to this platform or use the platform as a support for a sample in a container. Use an additional thread cross on top to hold the container in place.

3.1.3.2.2.1.4 Gelatin capsule

Gelatin capsules can be very useful for containing and mounting samples. Many aspects of using gelatin capsules have been mentioned in the section, Containing the Sample. It is best if the sample is mounted near the capsule's center, or if it completely fills the capsule. Use extra capsule parts to produce mirror symmetry. The thread cross is an excellent way of holding a capsule in place.

3.1.3.2.2.1.5 Thread mounting

Another method of sample mounting is attaching the sample to a thread that runs through the sample tube. The thread can be attached to the sample holder at the ends of the sample tube with tape, for example. This method can be very useful with flat samples, such as those on substrates, particularly when the field is in the plane of the film. Be sure to close the sample tube with caps.

- Mounting with a disc platform.
- Mounting on crossed threads.
- Long thread mounting.

3.1.3.2.2.2 Steps for inserting the sample

1. Cut off a small section of a clear plastic drinking straw. The section must be small enough to fit inside the straw.
2. Weigh and measure the sample.
3. Use plastic tweezers to place the sample inside the small straw segment. It is important to use plastic tweezers not metallic ones as these will contaminate the sample.
4. Place the small straw segment inside the larger one. It should be approximately in the middle of the large drinking straw.
5. Attach the straw to the sample rod which is used to insert the sample into the SQUID machine.
6. Insert the sample rod with the attached straw into the vertical insertion hole on top of the SQUID.

3.1.3.2.3 Centre the sample

The sample must be centered in the SQUID pickup coils to ensure that all coils sense the magnetic moment of the sample. If the sample is not centered, the coils read only part of the magnetic moment.

During a centering measurement the MPMS scans the entire length of the samples vertical travel path, and the MPMS reads the maximum number of data points. During centering there are a number of terms which need to be understood.

1. A scan length is the length of a scan of a particular sample which should usually try and be the maximum of the sample.
2. A sample is centered when it is in the middle of a scan length. The data points are individual voltage readings plotting response curves in centering scan data files.
3. Autotracking is the adjustment of a sample position to keep a sample centered in SQUID coils. Autotracking compensates for thermal expansion and contraction in a sample rod.

As soon as a centering measurement is initiated, the sample transport moves upward, carrying the sample through the pickup coils. While the sample moves through the coils, the MPMS measures the SQUID's response to the magnetic moment of the sample and saves all the data from the centering measurement.

After a centering plot is performed the plot is examined to determine whether the sample is centered in the SQUID pickup coils. The sample is centered when the part of the large, middle curve is within 5cm of the half-way point of the scan length.

The shape of the plot is a function of the geometry of the coils. The coils are wound in a way which strongly rejects interference from nearby magnetic sources and lets the MPMS function without a superconducting shield around the pickup coils.

3.1.3.2.4 Geometric considerations

To minimize background noise and stray field effects, the MPMS magnetometer pick-up coil takes the form of a second-order gradiometer. An important feature of this gradiometer is that moving a long, homogeneous sample through it produces no signal as long as the sample extends well beyond the ends of the coil during measurement.

As a sample holder is moved through the gradiometer pickup coil, changes in thickness, mass, density, or magnetic susceptibility produce a signal. Ideally, only the sample to be measured produces this change. A homogeneous sample that extends well beyond the pick-up coils does not produce a signal, yet a small sample does produce a signal. There must be a crossover between these two limits. The sample length (along the field direction) should not exceed 10 mm. In order to obtain the most accurate measurements, it is important to keep the sample susceptibility constant over its length; otherwise distortions in the SQUID signal (deviations from a dipole signal) can result. It is also important to keep the sample close to the magnetometer centerline to get the most accurate measurements. When the sample holder background contribution is similar in magnitude to the sample signal, the relative positions of the sample and the materials producing the background are important. If there is a spatial offset between the two along the magnet axis, the signal produced by the combined sample and background can be highly distorted and will not be characteristic of the dipole moment being measured.

Even if the signal looks good at one temperature, a problem can occur if either of the contributions are temperature dependent.

Careful sample positioning and a sample holder with a center, or plane, of symmetry at the sample (i.e. materials distributed symmetrically about the sample, or along the principal axis for a symmetry plane) helps eliminate problems associated with spatial offsets.

3.1.3.2.5 Containing the Sample

Keep the sample space of the MPMS magnetometer clean and free of contamination with foreign materials. Avoid accidental sample loss into the sample space by properly containing the sample in an appropriate

sample holder. In all cases it is important to close the sample holder tube with caps in order to contain a sample that might become unmounted. This helps avoid sample loss and subsequent damage during the otherwise unnecessary recovery procedure. Position caps well out of the sample-measuring region and introduce proper venting.

3.1.3.2.6 Sample preparation workspace

Work area cleanliness and avoiding sample contamination are very important concerns. There are many possible sources of contamination in a laboratory. Use diamond tools when cutting hard materials. Avoid carbide tools because of potential contamination by the cobalt binder found in many carbide materials. The best tools for preparing samples and sample holders are made of plastic, titanium, brass, and beryllium copper (which also has a small amount of cobalt). Tools labeled non-magnetic can actually be made of steel and often be made "magnetic" from exposure to magnetic fields. However, the main concern from these "non-magnetic" tools is contamination by the iron and other ferrous metals in the tool. It is important to have a clean white-papered workspace and a set of tools dedicated to mounting your own samples. In many cases, the materials and tools used can be washed in dilute acid to remove ferrous metal impurities. Follow any acid washes with careful rinsing with deionized water.

Powdered samples pose a special contamination threat, and special precautions must be taken to contain them. If the sample is highly magnetic, it is often advantageous to embed it in a low susceptibility epoxy matrix like Duco cement. This is usually done by mixing a small amount of diluted glue with the powder in a suitable container such as a gelatin capsule. Potting the sample in this way can keep the sample from shifting or aligning with the magnetic field. In the case of weaker magnetic samples, measure the mass of the glue after drying and making a background measurement. If the powdered sample is not potted, seal it into a container, and watch it carefully as it is cycled in the airlock chamber.

3.1.3.2.7 Pressure equalization

The sample space of the MPMS has a helium atmosphere maintained at low pressure of a few torr. An airlock chamber is provided to avoid contamination of the sample space with air when introducing samples into the sample space. By pushing the purge button, the airlock is cycled between vacuum and helium gas three times, then pumped down to its working pressure. During the cycling, it is possible for samples to be displaced in their holders, sealed capsules to explode, and sample holders to be deformed. Many of these problems can be avoided if the sample holder is properly ventilated. This requires placing holes in the sample holder, out of the measuring region that will allow any closed spaces to be opened to the interlock chamber.

3.1.3.2.8 Air-sensitive samples and liquid samples

When working with highly air-sensitive samples or liquid samples it is best to first seal the sample into a glass tube. NMR and EPR tubes make good sample holders since they are usually made of a high-quality, low-susceptibility glass or fused silica. When the sample has a high susceptibility, the tube with the sample can be placed onto a platform like those described earlier. When dealing with a low susceptibility sample, it is useful to rest the bottom of the sample tube on a length of the same type of glass tubing. By producing near mirror symmetry, this method gives a nearly constant background with position and provides an easy method for background measurement (i.e., measure the empty tube first, then measure with a sample). Be sure that the tube ends are well out of the measuring region.

When going to low temperatures, check to make sure that the sample tube will not break due to differential thermal expansion. Samples that will go above room temperature should be sealed with a reduced pressure in the tube and be checked by taking the sample to the maximum experimental temperature prior to loading it into the magnetometer. These checks are especially important when the sample may be corrosive, reactive, or valuable.

3.1.3.2.9 Oxygen contamination

This application note describes potential sources for oxygen contamination in the sample chamber and discusses its possible effects. Molecular oxygen, which undergoes an antiferromagnetic transition at about 43 K, is strongly paramagnetic above this temperature. The MPMS system can easily detect the presence of a small amount of condensed oxygen on the sample, which when in the sample chamber can interfere significantly with sensitive magnetic measurements. Oxygen contamination in the sample chamber is usually the result of leaks in the system due to faulty seals, improper operation of the airlock valve, outgassing from the sample, or cold samples being loaded.

3.1.3.3 Bibliography

- J. Bland, Thesis M. Phys (Hons)., 'A Mossbauer spectroscopy and magnetometry study of magnetic multilayers and oxides.' Oliver Lodge Labs, Dept. Physics, University of Liverpool.
- Quantum Design, Operating manual for the MPMS, 1999.
- R. L. Fagaly, *Review of Scientific Instruments*, 2006, **77**, 101101.

3.2 Raman Spectroscopy

3.2.1 Raman and Surface-Enhanced Raman Spectroscopy⁴

3.2.1.1 What is Raman spectroscopy?

Raman spectroscopy is a powerful tool for determining chemical species. As with other spectroscopic techniques, Raman spectroscopy detects certain interactions of light with matter. In particular, this technique exploits the existence of Stokes and Anti-Stokes scattering to examine molecular structure. When radiation in the near infrared (NIR) or visible range interacts with a molecule, several types of scattering can occur. Three of these can be seen in the energy diagram in Figure 3.26.

⁴This content is available online at <<http://cnx.org/content/m34528/1.1/>>.

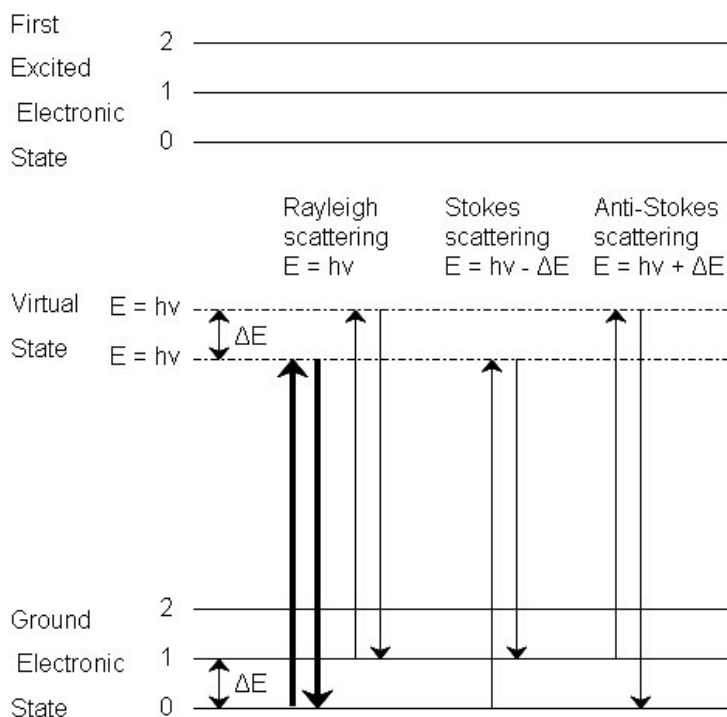


Figure 3.26: Three types of scattering by a molecule excited by a photon with energy $E = h\nu$. The most common transition is marked with bold arrows.

In all three types of scattering, an incident photon of energy $h\nu$ raises the molecule from a vibrational state to one of the infinite number of virtual states located between the ground and first electronic states. The type of scattering observed is dependent on how the molecule relaxes after excitation.

Rayleigh scattering

- Step 1. The molecule is excited to any virtual state.
- Step 2. The molecule relaxes back to its original state.
- Step 3. The photon is scattered elastically, leaving with its original energy.

Stokes scattering

- Step 1. The molecule is excited to any virtual state.
- Step 2. The molecule relaxes back to a higher vibrational state than it had originally.
- Step 3. The photon leaves with energy $h\nu - \Delta E$ and has been scattered inelastically.

Anti-Stokes scattering

- Step 1. The molecule begins in a vibrationally excited state.
- Step 2. The molecule is excited to any virtual state.
- Step 3. The molecule relaxes back to a lower vibrational state than it had originally.
- Step 4. The photon leaves with energy $h\nu + \Delta E$, and has been scattered superelastically.

Rayleigh scattering is by far the most common transition, due to the fact that no change has to occur in the vibrational state of the molecule. The anti-Stokes transition is the least common, as it requires the molecule to be in a vibrationally excited state before the photon is incident upon it. Due to the lack of intensity of the anti-Stokes signal and filtering requirements that eliminate photons with incident energy and higher, generally only Stokes scattering is used in Raman measurements. The relative intensities of Rayleigh, Stokes and anti-Stokes scattering can be seen in Figure 3.27.

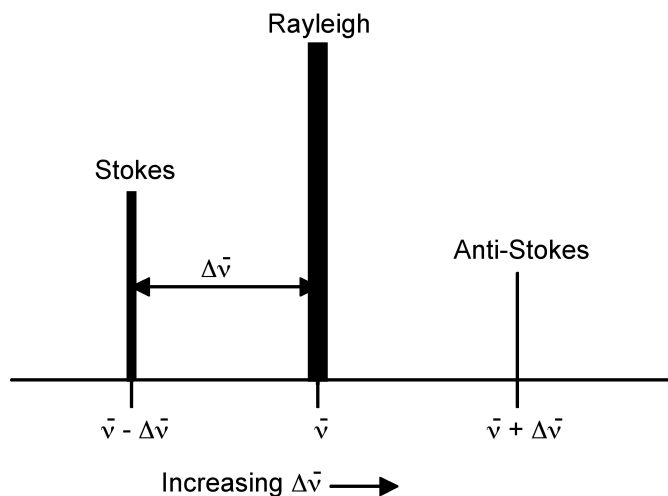


Figure 3.27: Location and relative intensity (indicated by peak height and width) of the Stokes and anti-Stokes scattering relative to Rayleigh scattering.

Raman spectroscopy observes the change in energy between the incident and scattered photons associated with the Stokes and anti-Stokes transitions. This is typically measured as the change in the wavenumber (cm^{-1}), from the incident light source. Because Raman measures the change in wavenumber, measurements can be taken using a source at any wavelength; however, near infrared and visible radiation are commonly used. Photons with ultraviolet wavelengths could work as well, but tend to cause photodecomposition of the sample.

3.2.1.2 Comparison between Raman and infrared spectroscopy

Raman spectroscopy sounds very much like infrared (IR) spectroscopy; however, IR examines the wavenumber at which a functional group has a vibrational mode, while Raman observes the shift in vibration from an incident source. The Raman frequency shift is identical to the IR peak frequency for a given molecule or functional group. As mentioned above, this shift is independent of the excitation wavelength, giving versatility to the design and applicability of Raman instruments.

The cause of the vibration is also mechanistically different between IR and Raman. This is because the two operate on different sets of selection rules. IR absorption requires a dipole moment or change in charge distribution to be associated with the vibrational mode. Only then can photons of the same energy as the vibrational state of molecule interact. A schematic of this can be seen in Figure 3.28.



Figure 3.28: A change in dipole moment is required for a vibrational mode to be IR active.

Raman signals, on the other hand, due to scattering, occur because of a molecule's polarizability, illustrated in Figure 3.29. Many molecules that are inactive or weak in the IR will have intense Raman signals. This results in often complementary techniques.

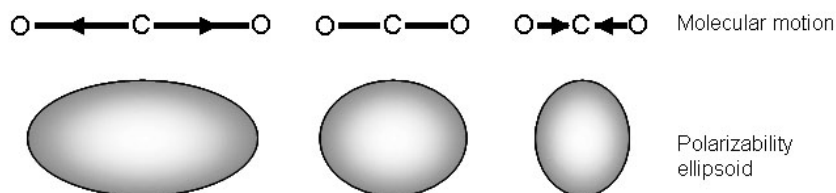


Figure 3.29: A change in the polarizability of a bond is required for a vibrational mode to be Raman active.

3.2.1.3 What does Raman spectroscopy measure?

Raman activity depends on the polarizability of a bond. This is a measure of the deformability of a bond in an electric field. This factor essentially depends on how easy it is for the electrons in the bond to be displaced, inducing a temporary dipole. When there is a large concentration of loosely held electrons in a bond, the polarizability is also large, and the group or molecule will have an intense Raman signal. Because of this, Raman is typically more sensitive to the molecular framework of a molecule rather than a specific functional group as in IR. This should not be confused with the polarity of a molecule, which is a measure of the separation of electric charge within a molecule. Polar molecules often have very weak Raman signals due to the fact that electronegative atoms hold electrons so closely.

Raman spectroscopy can provide information about both inorganic and organic chemical species. Many electron atoms, such as metals in coordination compounds, tend to have many loosely bound electrons, and therefore tend to be Raman active. Raman can provide information on the metal ligand bond, leading to knowledge of the composition, structure, and stability of these complexes. This can be particularly useful in metal compounds that have low vibrational absorption frequencies in the IR. Raman is also very useful for determining functional groups and fingerprints of organic molecules. Often, Raman vibrations are highly characteristic to a specific molecule, due to vibrations of a molecule as a whole, not in localized groups. The groups that do appear in Raman spectra have vibrations that are largely localized within the group, and often have multiple bonds involved.

3.2.1.4 What is surface-enhanced Raman spectroscopy?

Raman measurements provide useful characterization of many materials. However, the Raman signal is inherently weak (less than 0.001% of the source intensity), restricting the usefulness of this analytical tool. Placing the molecule of interest near a metal surface can dramatically increase the Raman signal. This is the basis of surface-enhanced Raman spectroscopy (SERS). There are several factors leading to the increase in Raman signal intensity near a metal surface.

1. The distance to the metal surface.
 - Signal enhancement drops off with distance from the surface.
 - The molecule of interest must be close to the surface for signal enhancement to occur.
2. Details about the metal surface: morphology and roughness.
 - This determines how close and how many molecules can be near a particular surface area.
3. The properties of the metal.
 - Greatest enhancement occurs when the excitation wavelength is near the plasma frequency of the metal.
4. The relative orientation of the molecule to the normal of the surface.
 - The polarizability of the bonds within the molecule can be affected by the electrons in the surface of the metal.

3.2.1.5 Bibliography

- W. Demtröder, *Laser Spectroscopy Basic Concepts and Instrumentation*, Springer, New York (2003).
- D. W. Mayo, F. A. Miller, and R. W. Hannah, *Course Notes on the Interpretation of Infrared and Raman Spectra*, Wiley-VCH, Hoboken, NJ (2003).
- D. A. Skoog, F. J. Holler, and S. R. Crouch, *Principles of Instrumental Analysis*, 6th edition, Brooks Cole (2006).

3.2.2 Characterization of Single-Walled Carbon Nanotubes by Raman Spectroscopy⁵

3.2.2.1 Introduction

Carbon nanotubes (CNTs) have proven to be a unique system for the application of Raman spectroscopy, and at the same time Raman spectroscopy has provided an exceedingly powerful tool useful in the study of the vibrational properties and electronic structures of CNTs. Raman spectroscopy has been successfully applied for studying CNTs at single nanotube level.

The large van der Waals interactions between the CNTs lead to an agglomeration of the tubes in the form of bundles or ropes. This problem can be solved by wrapping the tubes in a surfactant or functionalizing the SWNTs by attaching appropriate chemical moieties to the sidewalls of the tube. Functionalization causes a local change in the hybridization from sp^2 to sp^3 of the side-wall carbon atoms, and Raman spectroscopy can be used to determine this change. In addition information on length, diameter, electronic type (metallic or semiconducting), and whether nanotubes are separated or in bundle can be obtained by the use of Raman spectroscopy. Recent progress in understanding the Raman spectra of single walled carbon nanotubes (SWNT) have stimulated Raman studies of more complicated multi-wall carbon nanotubes (MWNT), but unfortunately quantitative determination of the latter is not possible at the present state of art.

⁵This content is available online at <<http://cnx.org/content/m22925/1.2/>>.

3.2.2.2 Characterizing SWNTs

Raman spectroscopy is a single resonance process, i.e., the signals are greatly enhanced if either the incoming laser energy (E_{laser}) or the scattered radiation matches an allowed electronic transition in the sample. For this process to occur, the phonon modes are assumed to occur at the center of the Brillouin zone ($q = 0$). Owing to their one dimensional nature, the Π -electronic density of states of a perfect, infinite, SWNTs form sharp singularities which are known as van Hove singularities (vHs), which are energetically symmetrical with respect to Fermi level (E_f) of the individual SWNTs. The allowed optical transitions occur between matching vHs of the valence and conduction band of the SWNTs, i.e., from first valence band vHs to the first conduction band vHs (E_{11}) or from the second vHs of the valence band to the second vHs of the conduction band (E_{22}). Since the quantum state of an electron (k) remains the same during the transition, it is referred to as k -selection rule.

The electronic properties, and therefore the individual transition energies in SWNTs are given by their structure, i.e., by their chiral vector that determines the way SWNT is rolled up to form a cylinder. Figure 3.30 shows a SWNT having vector R making an angle θ , known as the chiral angle, with the so-called zigzag or r_1 direction.

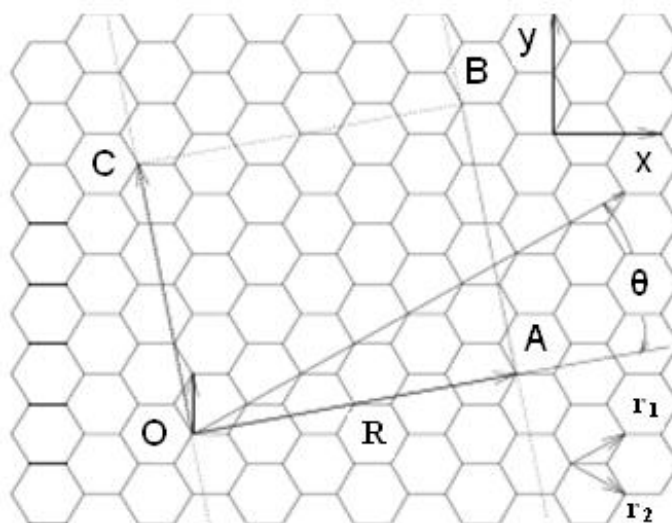


Figure 3.30: The unrolled honeycomb lattice of a nanotube. When the sites O and A, and the sites B and C are connected, a portion of a graphene sheet can be rolled seamlessly to form a SWNT. The vectors OA and OB define the chiral vector R of the nanotube, respectively. The rectangle OABC defines the unit cell if the nanotube. The figure is constructed for $(n,m) = (4,2)$ nanotube. Adapted from M. S. Dresselhaus, G. Dresselhaus, R. Saito, and A. Jorio, *Physics Reports*, 2004, **2**, 47.

Raman spectroscopy of an ensemble of many SWNTs having different chiral vectors is sensitive to the subset of tubes where the condition of allowed transition is fulfilled. A 'Kataura-Plot' gives the allowed electronic transition energies of individual SWNTs as a function of diameter d , hence information on which tubes are resonant for a given excitation wavelength can be inferred. Since electronic transition energies vary roughly as $1/d$, the question whether a given laser energy probes predominantly semiconducting or metallic tubes depends on the mean diameter and diameter distribution in the SWNT ensemble. However,

the transition energies that apply to an isolated SWNT do not necessarily hold for an ensemble of interacting SWNTs owing to the mutual van der Waals interactions.

Figure 3.31 shows a typical Raman spectrum from 100 to 3000 cm^{-1} taken of SWNTs produced by catalytic decomposition of carbon monoxide (HiPco-process). The two dominant Raman features are the radial breathing mode (RBM) at low frequencies and tangential (G-band) multifeature at higher frequencies. Other weak features, such as the disorder induced D-band and the G' band (an overtone mode) are also shown.

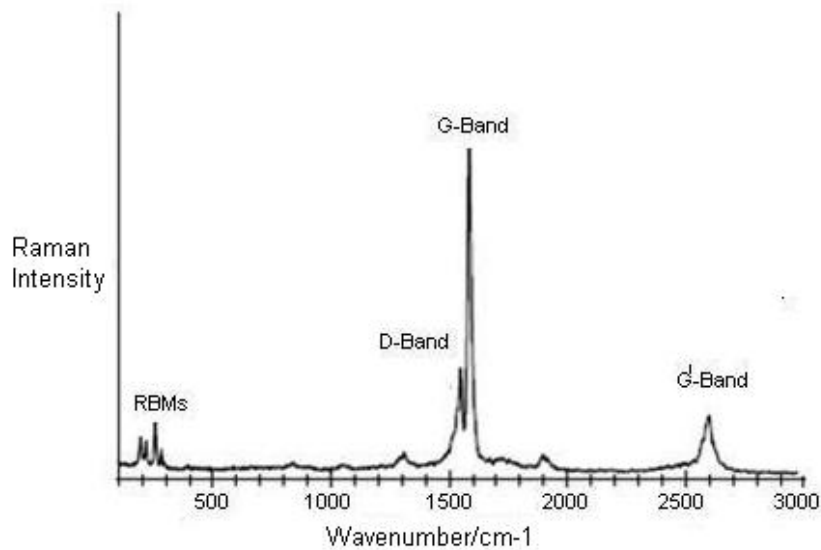


Figure 3.31: Raman spectrum of HiPco SWNTs using a laser of wavelength of $\lambda_{\text{exc}} = 633 \text{ nm}$. Adapted from R. Graupner, *J. Raman Spectrosc.*, 2007, **38**, 673.

3.2.2.3 Modes in the Raman spectra of SWNTs

3.2.2.3.1 Radial breathing modes (RBMs)

Out of all Raman modes observed in the spectra of SWNTs, the radial breathing modes are unique to SWNTs. They appear between $150 \text{ cm}^{-1} < \omega_{\text{RBM}} < 300 \text{ cm}^{-1}$ from the elastically scattered laser line. It corresponds to the vibration of the C atoms in the radial direction, as if the tube is breathing (Figure 3.32). An important point about these modes is the fact that the energy (or wavenumber) of these vibrational modes depends on the diameter (d) of the SWNTs, and not on the way the SWNT is rolled up to form a cylinder, i.e., they do not depend on the θ of the tube.

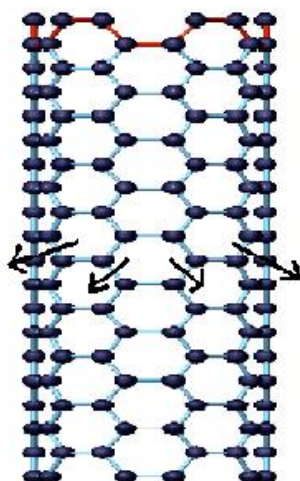


Figure 3.32: Schematic picture showing vibration for RBM. Adapted from A. Jorio, M. A. Pimenta, A. G. S. Filho, R. Saito, G. Dresselhaus, and M. S. Dresselhaus, *New J. Phys.*, 2003, **5**, 139.

These features are very useful for characterizing nanotube diameters through the relation $\omega_{\text{RBM}} = A/d + B$, where A and B are constants and their variations are often attributed to environmental effects, i.e., whether the SWNTs are present as individual tubes wrapped in a surfactant, isolated on a substrate surface, or in the form of bundles. However, for typical SWNT bundles in the diameter range, $d = 1.5 \pm 0.2$ nm, $A = 234 \text{ cm}^{-1} \text{ nm}$ and $B = 10 \text{ cm}^{-1}$ (where B is an upshift coming from tube-tube interactions). For isolated SWNTs on an oxidized Si substrate, $A = 248 \text{ cm}^{-1} \text{ nm}$ and $B = 0$. As can be seen from Figure 3.33, the relation $\omega_{\text{RBM}} = A/d + B$ holds true for the usual diameter range i.e., when d lies between 1 and 2 nm. However, for d less than 1 nm, nanotube lattice distortions lead to chirality dependence of ω_{RBM} and for large diameters tubes when, d is more than 2 nm the intensity of RBM feature is weak and is hardly observable.

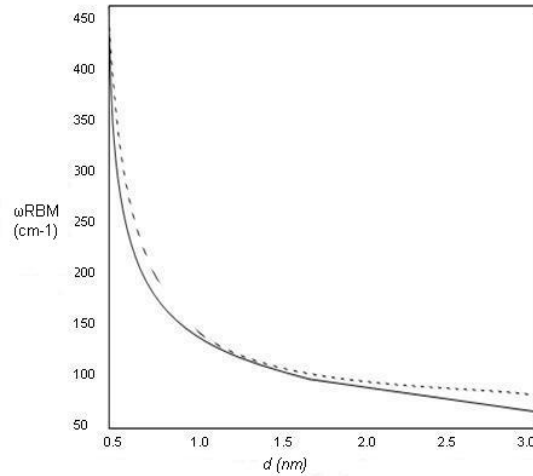


Figure 3.33: RBM frequencies $\omega_{\text{RBM}} = A/d + B$ versus nanotube diameter for (i) $A = 234 \text{ cm}^{-1} \text{ nm}$ and $B = 10 \text{ cm}^{-1}$, for SWNT bundles (dashed curve); (ii) $A = 248 \text{ cm}^{-1} \text{ nm}$ and $B = 0$, for isolated SWNTs (solid curve). Adapted from A. Jorio, M. A. Pimenta, A. G. S. Filho, R. Saito, G. Dresselhaus, and M. S. Dresselhaus, *New J. Phys.*, 2003, **5**, 139.

Hence, a single Raman measurement gives an idea of the tubes that are in resonance with the laser line, but does not give a complete characterization of the diameter distribution of the sample. However, by taking Raman spectra using many laser lines, a good characterization of the diameter distributions in the sample can be obtained. Also, natural line widths observed for isolated SWNTs are $\omega_{\text{RBM}} = 3 \text{ cm}^{-1}$, but as the tube diameter is increased, broadening is observed which is denoted by Γ_{RBM} . It has been observed that for $d > 2 \text{ nm}$, $\Gamma_{\text{RBM}} > 20 \text{ cm}^{-1}$. For SWNT bundles, the line width does not reflect Γ_{RBM} , it rather reflects an ensemble of tubes in resonance with the energy of laser.

3.2.2.3.1.1 Variation of RBM intensities upon functionalization

Functionalization of SWNTs leads to variations of relative intensities of RBM compared to the starting material (unfunctionalized SWNTs). Owing to the diameter dependence of the RBM frequency and the resonant nature of the Raman scattering process, chemical reactions that are sensitive to the diameter as well as the electronic structure, i.e., metallic or semiconducting of the SWNTs can be sorted out. The difference in Raman spectra is usually inferred by thermal defunctionalization, where the functional groups are removed by annealing. The basis of using annealing for defunctionalizing SWNTs is based on the fact that annealing restores the Raman intensities, in contrast to other treatments where a complete disintegration of the SWNTs occurs. Figure 3.34 shows the Raman spectra of the pristine, functionalized and annealed SWNTs. It can be observed that the absolute intensities of the radial breathing modes is drastically reduced after functionalization. This decrease can be attributed to vHs, which themselves are a consequence of translational symmetry of the SWNTs. Since the translational symmetry of the SWNTs is broken as a result of irregular distribution of the sp^3 -sites due to the functionalization, these vHs are broadened and strongly reduced in intensity. As a result, the resonant Raman cross section of all modes is strongly reduced as well.

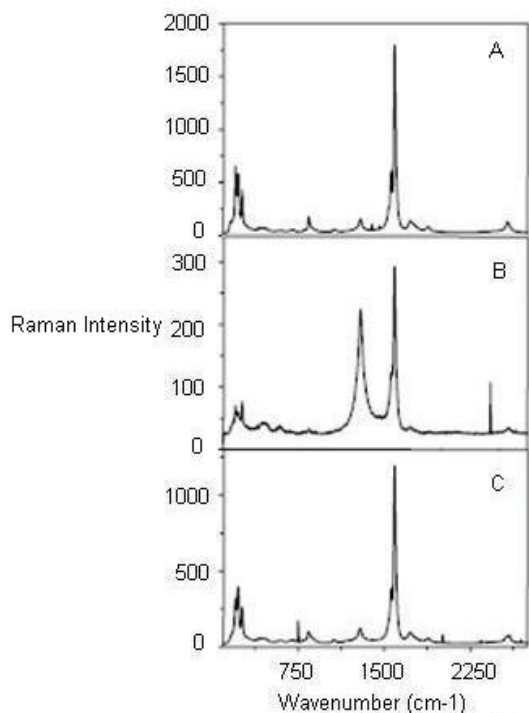


Figure 3.34: Raman spectra of sidewall functionalized SWNTs of (A) pristine material, (B) functionalized SWNTs, and (C) after annealing at 750 °C in Ar. Adapted from R. Graupner, *J. Raman Spectrosc.*, 2007, **38**, 673.

For an ensemble of functionalized SWNTs, a decrease in high wavenumber RBM intensities has been observed which leads to an inference that destruction of small diameter SWNT takes place. Also, after prolonged treatment with nitric acid and subsequent annealing in oxygen or vacuum, diameter enlargement of SWNTs is observed from the disappearance of RBMs from small diameter SWNTs and the appearance of new RBMs characteristic of SWNTs with larger diameters. In addition, laser irradiation seems to damage preferentially small diameter SWNTs. In all cases, the decrease of RBM intensities is either attributed to the complete disintegration of SWNTs or reduction in resonance enhancement of selectively functionalized SWNTs. However, change in RBM intensities can also have other reasons. One reason is doping induced bleaching of electronic transitions in SWNTs. When a dopant is added, a previously occupied electronic state can be filled or emptied, as a result of which E_f in the SWNTs is shifted. If this shift is large enough and the conduction band vHs corresponding to the respective E_{ii} transition that is excited by the laser light gets occupied (n-type doping) or the valence band vHs is emptied (p-type doping), the resonant enhancement is lost as the electronic transitions are quenched.

Sample morphology has also seen to affect the RBMs. The same unfunctionalized sample in different aggregation states gives rise to different spectra. This is because the transition energy, E_{ii} depends on the aggregation state of the SWNTs.

3.2.2.3.2 Tangential modes (G-band)

The tangential modes are the most intensive high-energy modes of SWNTs and form the so-called G-band, which is typically observed at around 1600 cm^{-1} . For this mode, the atomic displacements occur along the circumferential direction (Figure 3.35). Spectra in this frequency can be used for SWNT characterization, independent of the RBM observation. This multi-peak feature can, for example, also be used for diameter characterization, although the information provided is less accurate than the RBM feature, and it gives information about the metallic character of the SWNTs in resonance with laser line.

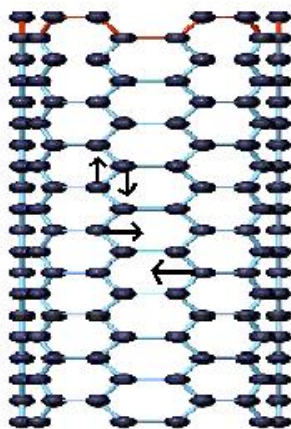


Figure 3.35: Schematic picture showing the atomic vibrations for the G-band. Adapted from A. Jorio, M. A. Pimenta, A. G. S. Filho, R. Saito, G. Dresselhaus, and M. S. Dresselhaus, *New J. Phys.*, 2003, **5**, 139.

The tangential modes are useful in distinguishing semiconducting from metallic SWNTs. The difference is evident in the G- feature (Figure 3.36 and Figure 3.37) which broadens and becomes asymmetric for metallic SWNTs in comparison with the Lorentzian lineshape for semiconducting tubes, and this broadening is related to the presence of free electrons in nanotubes with metallic character. This broadened G-feature is usually fit using a Breit-Wigner-Fano (BWF) line that accounts for the coupling of a discrete phonon with a continuum related to conduction electrons. This BWF line is observed in many graphite-like materials with metallic character, such as n-doped graphite intercalation compounds (GIC), n-doped fullerenes, as well as metallic SWNTs. The intensity of this G- mode depends on the size and number of metallic SWNTs in a bundle (Figure 3.38).

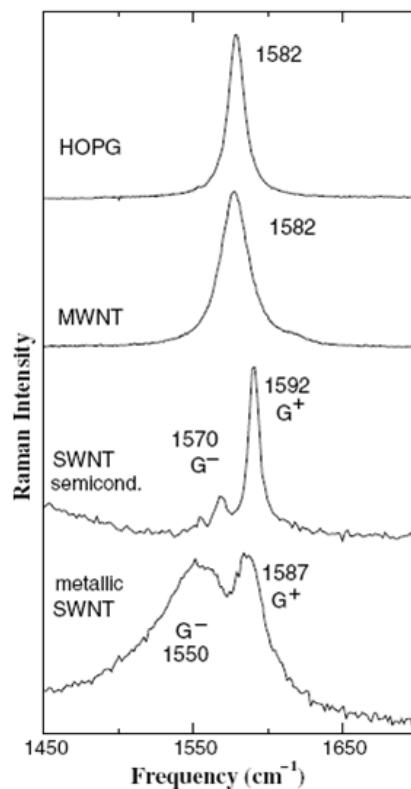


Figure 3.36: G-band for highly ordered pyrolytic graphite (HOPG), MWNT bundles, one isolated semiconducting SWNT and one isolated metallic SWNT. The multi-peak G-band feature is not clear for MWNTs due to the large tube size. A. Jorio, M. A. Pimenta, A. G. S. Filho, R. Saito, G. Dresselhaus, and M. S. Dresselhaus, *New J. Phys.*, 2003, **5**, 139. Copyright Institute of Physics (2005).

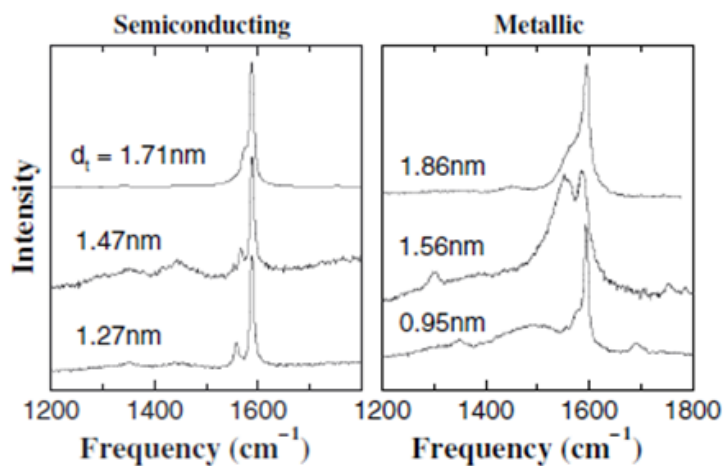


Figure 3.37: Raman signal from three isolated semiconducting and three isolated metallic SWNTs showing the G-and D-band profiles. SWNTs in good resonance (strong signal with low signal to noise ratio) show practically no D-band. A. Jorio, M. A. Pimenta, A. G. S. Filho, R. Saito, G. Dresselhaus, and M. S. Dresselhaus, *New J. Phys.*, 2003, **5**, 139. Copyright Institute of Physics (2005).

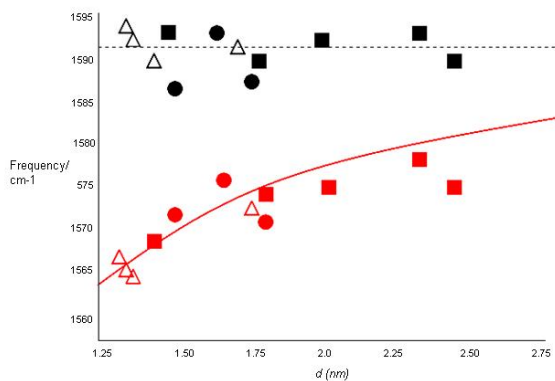


Figure 3.38: Dependence of G+ (black symbols) and G- (red symbols) frequencies as a function of diameter. Adapted from M. Paillet, T. Michel, J. C. Meyer, V. N. Popov, L. Henrad, S. Roth, and J. L. Sauvajol, *Phy. Rev. Lett.*, 2006, **96**, 257401.

3.2.2.3.2.1 Change of G-band line shape on functionalization

Chemical treatments are found to affect the line shape of the tangential line modes. Selective functionalization of SWNTs or a change in the ratio of metallic to semiconducting SWNTs due to selective etching is responsible for such a change. According to Figure 3.39, it can be seen that an increase or decrease of the BWF line shape is observed depending on the laser wavelength. At $\lambda_{\text{exc}} = 633$ nm, the preferentially functionalized small diameter SWNTs are semiconducting, therefore the G-band shows a decrease in the BWG asymmetry. However, the situation is reversed at 514 nm, where small metallic tubes are probed. BWF resonance intensity of small bundles increases with bundle thickness, so care should be taken that the effect ascribed directly to functionalization of the SWNTs is not caused by the exfoliation of the previously bundles SWNT.

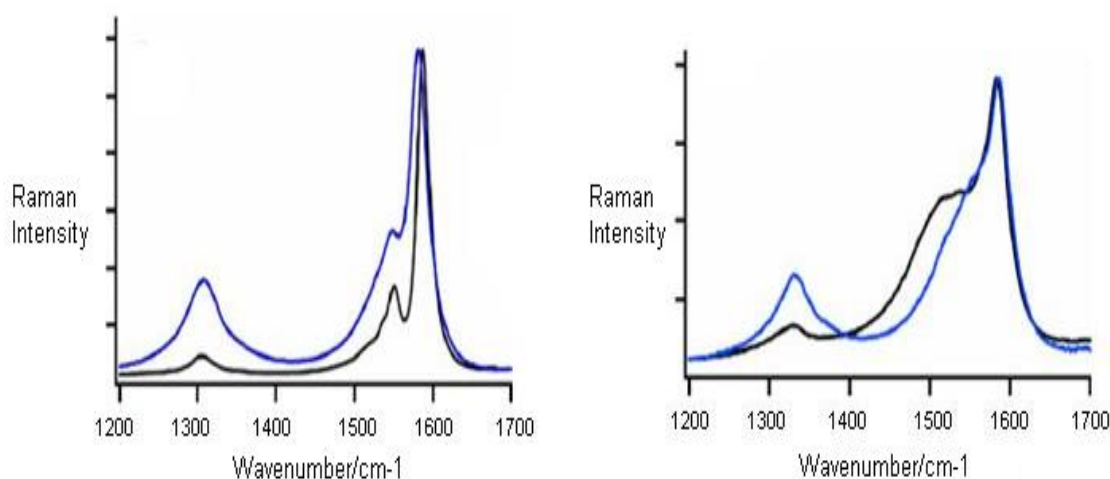


Figure 3.39: G-and D-band spectra of pristine (black) and ozonized (blue) SWNTs at 633 nm (left) and 514 nm (right) excitation. Adapted from R. Graupner, *J. Raman Spectrosc.*, 2007, **38**, 673.

3.2.2.3.3 Disorder-induced D-band

This is one of the most discussed modes for the characterization of functionalized SWNTs and is observed at $1300\text{--}1400\text{ cm}^{-1}$. Not only for functionalized SWNTs, D-band is also observed for unfunctionalized SWNTs. From a large number of Raman spectra from isolated SWNTs, about 50% exhibit observable D-band signals with weak intensity (Figure 3.37). A large D-peak compared with the G-peak usually means a bad resonance condition, which indicates the presence of amorphous carbon.

The appearance of D-peak can be interpreted due to the breakdown of the k-selection rule. It also depends on the laser energy and diameter of the SWNTs. This behavior is interpreted as a double resonance effect, where not only one of the direct, k-conserving electronic transitions, but also the emission of phonon is a resonant process. In contrast to single resonant Raman scattering, where only phonons around the center of the Brillouin zone ($q = 0$) are excited, the phonons that provoke the D-band exhibit a non-negligible q vector. This explains the double resonance theory for D-band in Raman spectroscopy. In few cases, the overtone of the D-band known as the G'-band (or D*-band) is observed at $2600\text{--}2800\text{ cm}^{-1}$, and it does not

require defect scattering as the two phonons with q and $-q$ are excited. This mode is therefore observed independent of the defect concentration.

The presence of D-band cannot be correlated to the presence of various defects (such as hetero-atoms, vacancies, heptagon-pentagon pairs, kinks, or even the presence of impurities, etc). Following are the two main characteristics of the D-band found in carbon nanotubes:

1. Small linewidths: Γ_D values for SWNTs range from 40 cm^{-1} down to 7 cm^{-1} .
2. Lower frequencies: D-band frequency is usually lower than the frequency of sp^2 -based carbons, and this downshift of frequency shows $1/d$ dependence.

3.2.2.3.3.1 D-Band intensity as a measure of functionalization versus defect density

Since D-peak appears due to the presence defects, an increase in the intensity of the band is taken as a fingerprint for successful functionalization. But, whether D-band intensity is a measure of degree of functionalization or not is still sure. So, it is not correct to correlate D-peak intensity or D-peak area to the degree of functionalization. From Figure 3.40, it can be observed that for lower degree of functionalization, intensity of the D-band scales linearly with defect density. As the degree of functionalization is further increased, both D and G-band area decrease, which is explained by the loss of resonance enhancement due to functionalization. Also, normalization of the D-peak intensity to the G-band in order to correct for changes in resonance intensities also leads to a decrease for higher densities of functional groups.

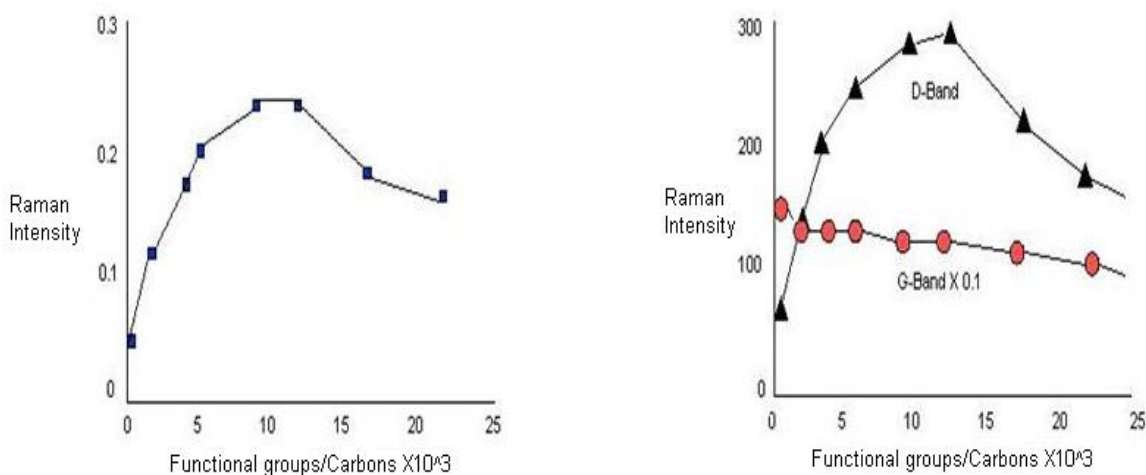


Figure 3.40: The left figure shows the intensity ratio I_D/I_G and the right figure shows D- and G-band intensity at $\lambda_{\text{exc}} = 532\text{ nm}$ with respect to degree of functionalization using diazonium reagents. Adapted from R. Graupner, *J. Raman Spectrosc.*, 2007, **38**, 673.

3.2.2.3.4 Limitations of Raman spectroscopy

Though Raman spectroscopy has provides an exceedingly important tool for characterization of SWNTs, however, it suffers from few serious limitations. One of the main limitations of Raman spectroscopy is that it does not provide any information about the extent of functionalization in the SWNTs. The presence of

D-band indicates disorder, i.e. side wall distribution, however it cannot differentiate between the number of substituents and their distribution. Following are the two main limitations of Raman Spectroscopy:

3.2.2.3.4.1 Quantification of substituents

This can be illustrated by the following examples. Purified HiPco tubes may be fluorinated at 150 °C to give F-SWNTs with a C:F ratio of approximately 2.4:1. The Raman spectra (using 780 nm excitation) for F-SWNTs shows in addition to the tangential mode at $\sim 1587\text{ cm}^{-1}$ an intense broad D (disorder) mode at $\sim 1295\text{ cm}^{-1}$ consistent with the side wall functionalization. Irrespective of the arrangements of the fluorine substituents, thermolysis of F-SWNTs results in the loss of fluorine and the re-formation of unfunctionalized SWNTs along with their cleavage into shorter length tubes. As can be seen from Figure 3.41, the intensity of the D-band decreases as the thermolysis temperature increases. This is consistent with the loss of F-substituents. The G-band shows a concomitant sharpening and increase in intensity.

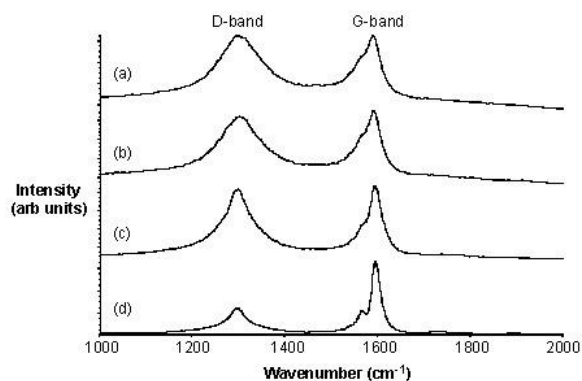


Figure 3.41: Raman spectra of F-SWNTs (a) as prepared at 150 °C and after heating to (b) 400, (c) 450 and (d) 550 °C.

As discussed above, the presence of a significant D mode has been the primary method for determining the presence of sidewall functionalization. It has been commonly accepted that the relative intensity of the D mode *versus* the tangential G mode is a quantitative measure of level of substitution. However, as discussed below, the G:D ratio is also dependent on the distribution of substituents. Using Raman spectroscopy in combination with XPS analysis of F-SWNTs that have been subjected to thermolysis at different temperatures, a measure of the accuracy of Raman as a quantitative tool for determining substituent concentration can be obtained. As can be seen from Figure 3.42, there is essentially no change in the G:D band ratio despite a doubling amount of functional groups. Thus, at low levels of functionalization the use of Raman spectroscopy to quantify the presence of fluorine substituents is a clearly suspect.

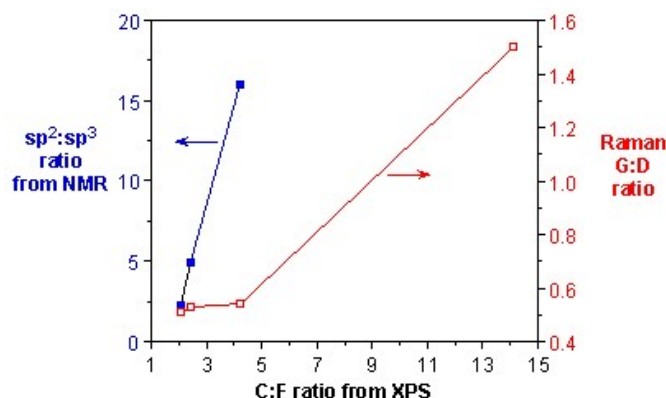


Figure 3.42: C(sp²):C-F(sp³) ratio (blue) and Raman G-band:D-band ratio (red) as a function of C:F ratio from XPS.

On the basis of above data it can be concluded that Raman spectroscopy does not provide an accurate quantification of small differences at low levels of functionalization, whereas when a comparison between samples with high levels of functionalization or large differences in degree of functionalization is required, Raman spectroscopy provides a good quantification.

3.2.2.3.4.2 Number versus distribution

Fluorinated nanotubes may be readily functionalized by reaction with the appropriate amine in the presence of base according to the scheme shown in Figure 3.43.

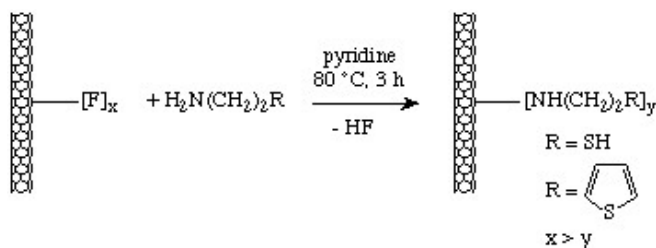


Figure 3.43: Synthesis of functionalized SWNTs.

When the Raman spectra of the functionalized SWNTs is taken (Figure 3.44), it is found out that the relative intensity of the disorder D-band at $\sim 1290\text{ cm}^{-1}$ versus the tangential G-band ($1500 - 1600\text{ cm}^{-1}$) is much higher for thiophene-SWNT than thiol-SWNT. If the relative intensity of the D mode is the measure of the level of substitution, it can be concluded that there are more number of thiophene groups present per C than thiol groups. However, from the TGA weight loss data the SWNT-C:substituent ratios are calculated to be 19:1 and 17.5:1. Thus, contrary to the Raman data the TGA suggest that the number of substituents per C (in the SWNT) is actually similar for both substituents.

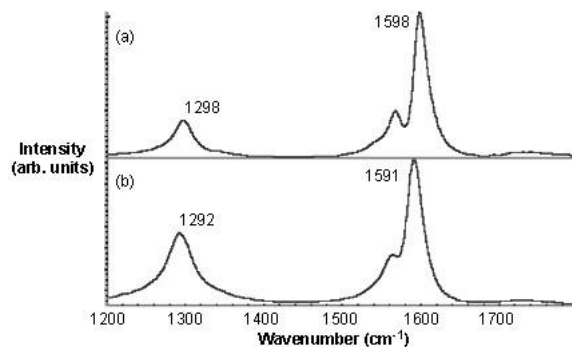


Figure 3.44: Raman spectrum of (a) thiol-SWNT and (b) thiophene-SWNT using 780 nm excitation showing the relative intensity of D-band at $\sim 1300\text{ cm}^{-1}$ versus the G-band at $\sim 1590\text{ cm}^{-1}$.

This result would suggest that Raman spectroscopy is potentially unsuccessful in correctly providing the information about the number of substituents on the SWNTs. Subsequent imaging of the functionalized SWNTs by STM showed that the distribution of the functional groups was the difference between the thiol and thiophene functionalized SWNTs Figure 3.45. Thus, relative ratio of the D- and G-bands is a measure of concentration and distribution of functional groups on SWNTs.

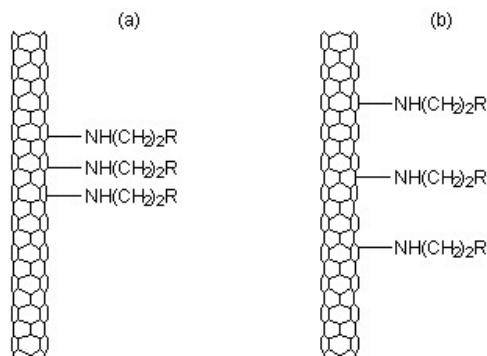


Figure 3.45: Schematic representation of the functional group distribution for (a) thiol-SWNT and (b) thiophene-SWNT.

3.2.2.4 Multi-walled carbon nanotubes (MWNTs)

Most of the characteristic differences that distinguish the Raman spectra in SWNTs from the spectra of graphite are not so evident for MWNTs. It is because the outer diameter for MWNTs is very large and the ensemble of CNTs in them varies from small to very large. For example, the RBM Raman feature associated with a small diameter inner tube (less than 2 nm) can sometimes be observed when a good resonance condition is established, but since the RBM signal from large diameter tubes is usually too weak

to be observable and the ensemble average of inner tube diameter broadens the signal, a good signal is not observed. However, when hydrogen gas in the arc discharge method is used, a thin innermost nanotube within a MWNT of diameter 1 nm can be obtained which gives strong RBM peaks in the Raman spectra.

Thereas the G+ - G- splitting is large for small diameter SWNT, the corresponding splitting of the G-band in MWNTs is both small in intensity and smeared out due to the effect of the diameter distribution. Therefore the G-band feature predominantly exists a weakly asymmetric characteristic lineshape, and a peak appearing close to the graphite frequency of 1582 cm^{-1} . however for isolated MWNTs prepared in the presence of hydrogen gas using the arc discharge method, it is possible to observe multiple G-band splitting effects even more clearly than for the SWNTs, and this is because environmental effects become relatively small for the innermost nanotube in a MWNT relative to the interactions occurring between SWNTs and different environments. The Raman spectroscopy of MWNTs has not been well investigated up to now. The new directions in this field are yet to be explored.

3.2.2.5 Bibliography

- R. Graupner, *J. Ramn Spectrosc.*, 2007, **38**, 673.
- S. Costa, B. Palen, M. Kruszynska, A. Bachmatiuk, and R.J. Kalenczuk, *Mat. Sci. Poland*, 2008, **26**, 433.
- M. Paillet, T. Michel, J. C. Meyer, V. N. Popov, L. Henrad, S. Roth, and J. L. Sauvajol, *Phy. Rev. Lett.*, 2006, **96**, 257401.
- L. Zhang, J. Zhang, N. Schmandt, J. Cratty, V. N. Khabashesku, K. F. Kelly, and A. R. Barron, *Chem. Commun.*, 2005, 5429.
- L. B. Alemany, L. Zhang, L. Zeng, C. L. Edwards, and A. R. Barron, *Chem. Mater.*, 2006, **19**, 735.
- M. S. Dresselhaus, G. Dresselhaus, R. Saito, and A. Jorio, *J. Phys. Rep.*, 2005, **2**, 47.
- A. Jorio, M. A. Pimenta, A. G. S. Filho, R. Saito, G. Dresselhaus, and M. S. Dresselhaus, *New J. Phys.*, 2003, **5**, 139.

3.2.3 Surface-Enhanced Raman Spectroscopy for the Study of Surface Chemistry⁶

The ever-rising interest in nanotechnology involves the synthesis and application of materials with a very high surface area to volume ratio. This places increasing importance on understanding the chemistry occurring at a surface, particularly the surface of a nanoparticle. Slight modifications of the nanoparticle or its surrounding environment can greatly affect many properties including the solubility, biological toxicity, and reactivity of the nanomaterial. Noble metal nanomaterials are of particular interest due to their unique optical properties and biological inertness.

One tool employed to understand the surface chemistry of noble metal nanomaterial, particularly those composed of gold or silver is *surface-enhanced Raman spectroscopy* (SERS). Replacing a metal surface with a metal nanoparticle increases the available surface area for the adsorption of molecules. Compared to a flat metal surface, a similar sample size using nanoparticles will have a dramatically stronger signal, since signal intensity is directly related to the concentration of the molecule of interest. Due to the shape and size of the structure, the electrons in the nanoparticle oscillate collectively when exposed to incident electromagnetic radiation. This is called the *localized surface plasmon resonance* (LSPR) of the nanoparticle. The LSPR of the nanoparticles boosts the Raman signal intensity dramatically for molecules of interest near the surface of the nanoparticle. In order to maximize this effect, a nanoparticle should be selected with its resonant wavelength falling in the middle of the incident and scattered wavelengths.

The overall intensity enhancement of SERS can be as large as a factor of 10^6 , with the surface plasmon resonance responsible for roughly four orders of magnitude of this signal increase. The other two orders of magnitude have been attributed to chemical enhancement mechanisms arising charge interactions between the metal particle and the adsorbate or from resonances in the adsorbate alone, as discussed above.

⁶This content is available online at <<http://cnx.org/content/m34522/1.1/>>.

3.2.3.1 Why is SERS useful for studying surface chemistry?

Traditionally, SERS uses nanoparticles made of conductive materials, such as gold, to learn more about a particular molecule. However, of interest in many growing fields that incorporate nanotechnology is the structure and functionalization of a nanoparticle stabilized by some surfactant or capping agent. In this case, SERS can provide valuable information regarding the stability and surface structure of the nanoparticle. Another use of nanoparticles in SERS is to provide information about a ligand's structure and the nature of ligand binding. In many applications it is important to know whether a molecule is bound to the surface of the nanoparticle or simply electrostatically interacting with it.

3.2.3.2 Sample preparation and instrumental details

The standard Raman instrument is composed of three major components. First, the instrument must have an illumination system. This is usually composed of one or more lasers. The major restriction for the illumination system is that the incident frequency of light must not be absorbed by the sample or solvent. The next major component is the sample illumination system. This can vary widely based on the specifics of the instrument, including whether the system is a standard macro-Raman or has micro-Raman capabilities. The sample illumination system will determine the phase of material under investigation. The final necessary piece of a Raman system is the spectrometer. This is usually placed 90° away from the incident illumination and may include a series of filters or a monochromator. An example of a macro-Raman and micro-Raman setup can be seen in Figure 3.46 and Figure 3.47. A macro-Raman spectrometer has a spatial resolution anywhere from $100\text{ }\mu\text{m}$ to one millimeter while a micro-Raman spectrometer uses a microscope to magnify its spatial resolution.

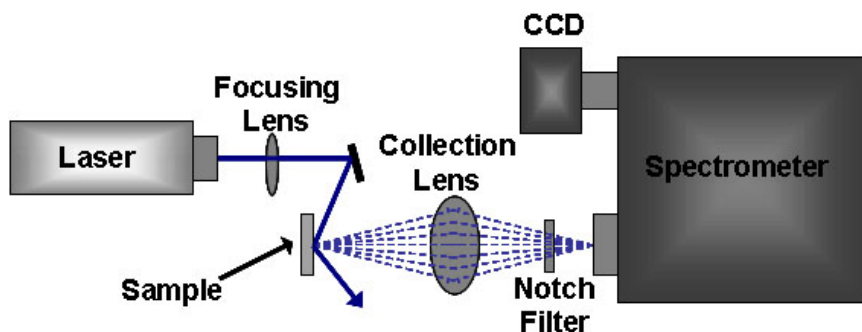


Figure 3.46: Schematic of a macro-Raman spectrometer.

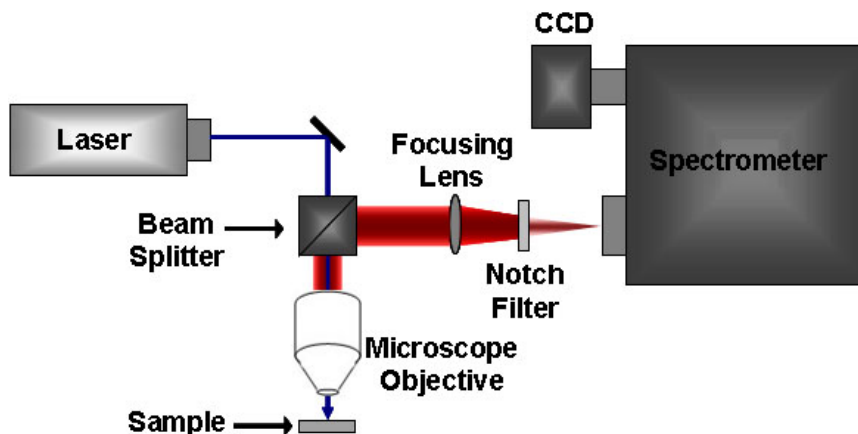


Figure 3.47: Schematic of a micro-Raman spectrometer where illumination and collection are performed through microscope objective.

3.2.3.3 Bibliography

- D. A. Skoog, F. J. Holler, and S. R. Crouch, *Principles of Instrumental Analysis*, 6th Ed, Brooks Cole (2006).
- P. L. Stiles, J. A. Dieringer, N. C. Shah, and R. P. van Duyne, *Annu. Rev. Anal. Chem.*, 2008, **1**, 601.

3.3 IR Spectroscopy

3.3.1 IR Sample Preparation: A Practical Guide⁷

3.3.1.1 Introduction

Infrared spectroscopy is based on molecular vibrations caused by the oscillation of molecular dipoles. Bonds have characteristic vibrations depending on the atoms in the bond, the number of bonds and the orientation of those bonds with respect to the rest of the molecule. Thus, different molecules have specific spectra that can be collected for use in distinguishing products or identifying an unknown substance (to an extent.)

Collecting spectra through this method goes about one of three general ways. Nujol mulls and pressed pellets are typically used for collecting spectra of solids, while thin-film cells are used for solution-phase IR spectroscopy. Spectra of gases can also be obtained but will not be discussed in this guide.

3.3.1.2 Infrared optical materials and handling

While it is all well and wonderful that substances can be characterized in this fashion one still has to be able to hold the substances inside of the instrument and properly prepare the samples. In an infrared spectrometer (Figure 3.48) the sample to be analyzed is held in front of an infrared laser beam, in order to do this, the sample must be contained in something, consequently this means that the very container the sample is in will absorb some of the infrared beam.

⁷This content is available online at <<http://cnx.org/content/m43564/1.1/>>.

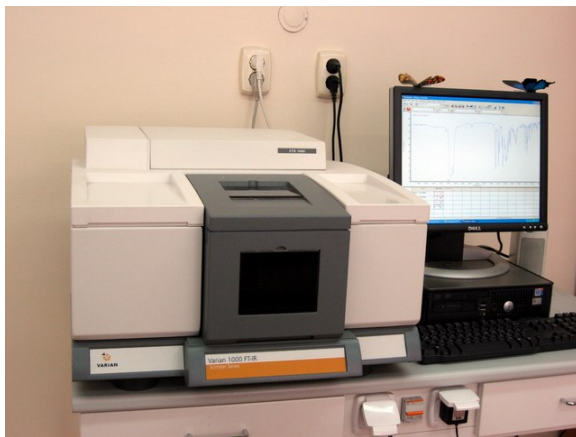


Figure 3.48: An example of a modern benchtop FT-IR spectrometer (Varian Corp.)

This is made somewhat complicated by the fact that all materials have some sort of vibration associated with them. Thus, if the sample holder has an optical window made of something that absorbs near where your sample does, the sample might not be distinguishable from the optical window of the sample holder. The range that is not blocked by a strong absorbance is known as a *window* (not to be confused with the optical materials of the cell.)

Windows are an important factor to consider when choosing the method to perform an analysis, as seen in Table 3.1 there are a number of different materials each with their own characteristic absorption spectra and chemical properties. Keep these factors in mind when performing analyses and precious sample will be saved. For most organic compounds NaCl works well though it is susceptible to attack from moisture. For metal coordination complexes KBr, or CsI typically work well due to their large windows. If money is not a problem then diamond or sapphire can be used for plates.

Material	Transparent Ranges (cm^{-1})	Solubility	Notes
NaCl	40,000 – 625	H_2O	Easy to polish, hygroscopic
Silica glass	55,000 – 3,000	HF	Attacked by HF
Quartz	40,000 – 2,500	HF	Attacked by HF
Sapphire	20,000 – 1,780	-	Strong
Diamond	40,000 – 2,500 and 1,800 – 200	-	Very strong, expensive, hard, useless for pellets.

continued on next page

CaF ₂	70,000 – 1,110	Acids	Attacked by acids, avoid ammonium salts.
BaF ₂	65,000 – 700	-	Avoid ammonium salts
ZnSe	10,000 – 550	Acids	Brittle, attacked by acids
AgCl	25,000 – 400	-	Soft, sensitive to light.
KCl	40,000 – 500	H ₂ O, Et ₂ O, acetone	
KBr	40,000 – 400	H ₂ O, EtOH	Hygroscopic, soft, easily polished, commonly used in making pellets.
CsBr	10,000 – 250	H ₂ O, EtOH, acetone	Hygroscopic, soft.
CsI	10,000 – 200	H ₂ O, EtOH, MeOH, acetone	Hygroscopic, soft.
Teflon	5,000 - 1,200, 1,200 – 900	-	Inert, disposable
Polyethylene	4,000 - 3,000, 2,800 - 1,460, 1,380 - 730, 720 - 30	-	Inert, disposable

Table 3.1: Various IR-transparent materials and their solubilities and other notes. M. R. Derrick, D. Stulik, and J. M. Landry, in *Scientific Tools in Conservation: Infrared Spectroscopy in Conservation Science*. Getty Conservation Institute (1999).

Proper handling of these plates will ensure they have a long, useful life. Here follows a few simple pointers on how to handle plates:

- Avoid contact with solvents that the plates are soluble in.
- Keep the plates in a dessicator, the less water the better, even if the plates are insoluble to water.
- Handle with gloves, clean gloves.
- Avoid wiping the plates to prevent scratching.

That said, these simple guidelines will likely reduce most damage that can occur to a plate by simply holding it other faults such as dropping the plate from a sufficient height can result in more serious damage.

3.3.1.3 Preparation of nujol mulls

A common method of preparing solid samples for IR analysis is mulling. The principle here is by grinding the particles to below the wavelength of incident radiation that will be passing through there should be limited scattering. To suspend those tiny particles, an oil, often referred to as Nujol is used. IR-transparent salt plates are used to hold the sample in front of the beam in order to acquire data. To prepare a sample for IR analysis using a salt plate, first decide what segment of the frequency band should be studied, refer to Table 3.1 for the materials best suited for the sample. Figure 3.49 shows the materials needed for preparing a mull.



Figure 3.49: In this photograph, the sample, ferrocene, two clean and polished KBr plates, an agate mortar and pestle, a mounting card and a spatula are displayed as the base minimum requirements for preparing a sample through a Nujol mull. Of course, a small bottle of mineral oil is also necessary.

Preparing the mull is performed by taking a small portion of sample and adding approximately 10% of the sample volume worth of the oil and grinding this in an agate mortar and pestle as demonstrated in Figure 3.50. The resulting mull should be transparent with no visible particles.



Figure 3.50: Mulling ferrocene into mineral oil with a mortar and pestle.

Another method involves dissolving the solid in a solvent and allowing it to dry in the agate pestle. If using this method ensure that all of the solvent has evaporated since the solvent bands will appear in the spectrum. Some gentle heating may assist this process. This method creates very fine particles that are of a relatively consistent size. After addition of the oil further mixing (or grinding) may be necessary.

Plates should be stored in a desiccator to prevent erosion by atmospheric moisture and should appear roughly transparent. Some materials such as silicon will not, however. Gently rinse the plates with hexanes to wash any residual material off of the plates. Removing the plates from the desiccator and cleaning them should follow the preparation of the mull in order to maintain the integrity of the salt plates. Of course, if the plate is not soluble in water then it is still a good idea just to prevent the threat of mechanical trauma or a stray jet of acetone from a wash bottle.

Once the mull has been prepared, add a drop to one IR plate (Figure 3.51), place the second plate on top of the drop and give it a quarter turn in order to evenly coat the plate surface as seen in Figure 3.52. Place it into the spectrometer and acquire the desired data.

NOTE: Always handle with gloves and preferably away from any sinks, faucets, or other sources of running or spraying water.



Figure 3.51: The prepared mull from an agate mortar and pestle being applied to a polished KBr plate.



Figure 3.52: Sandwiched KBr plates with a Nujol mull of ferrocene.

NOTE: Spectra acquired by this method will have strong C-H absorption bands throughout several ranges $3,000 - 2,800\text{ cm}^{-1}$ and $1,500 - 1,300\text{ cm}^{-1}$ and may obscure signal.

Cleaning the plate is performed as previously mentioned with hexanes or chloroform can easily be performed by rinsing and leaving them to dry in the hood. Place the salt plates back into the desiccator as soon as reasonably possible to prevent damage. It is highly advisable to polish the plates after use, no scratches, fogging, or pits should be visible on the face of the plate. Chips, so long as they don't cross the center of the plate are survivable but not desired. The samples of damaged salt plates in Figure 3.53 show common problems associated with use or potentially mishandling. Clouding, and to an extent, scratches can be polished out with an iron rouge. Areas where the crystal lattice is disturbed below the surface are impossible to fix and chips cannot be reattached.

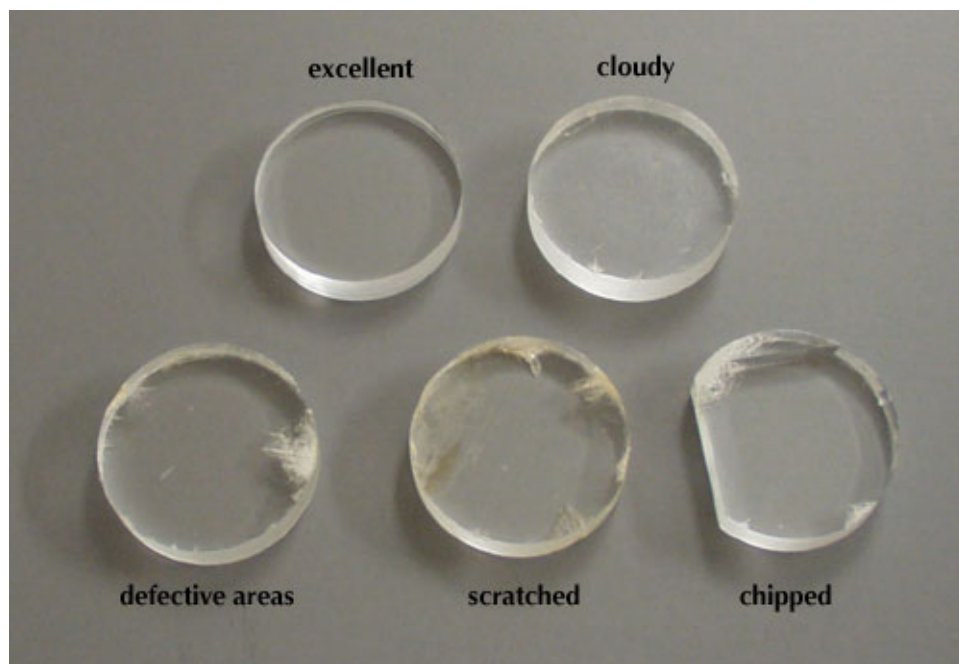


Figure 3.53: A series of plates indicating various forms of physical damage with a comparison to a good plate (Copyright: Colorado University-Boulder).

3.3.1.4 Preparation of pellets

In an alternate method, this technique is along the same lines of the nujol mull except instead of the suspending medium being mineral oil, the suspending medium is a salt. The solid is ground into a fine powder with an agate mortar and pestle with an amount of the suspending salt. Preparing pellets with diamond for the suspending agent is somewhat illadvised considering the great hardness of the substance. Generally speaking, an amount of KBr or CsI is used for this method since they are both soft salts. Two approaches can be used to prepare pellets, one is somewhat more expensive but both usually yield decent results.

The first method is the use of a press. The salt is placed into a cylindrical holder and pressed together with a ram such as the one seen in (Figure 3.54). Afterwards, the pellet, in the holder, is placed into the instrument and spectra acquired.



Figure 3.54: A large benchtop hydraulic press (Specac Inc.)

An alternate, and cheaper method requires the use of a large hex nut with a 0.5 inch inner diameter, two bolts, and two wrenches such as the kit seen in Figure 3.55. Step-by-step instructions for loading and using the press follows:

1. Screw one of the bolts into the nut about half way.
2. Place the salt pellet mixture into the other opening of the nut and level by tapping the assembly on a countertop.
3. Screw in the second bolt and place the assembly on its side with the bolts parallel to the countertop. Place one of the wrenches on the bolt on the right side with the handle aiming towards yourself.
4. Take the second wrench and place it on the other bolt so that it attaches with an angle from the table of about 45 degrees.
5. The second bolt is tightened with a body weight and left to rest for several minutes. Afterwards, the bolts are removed, and the sample placed into the instrument.

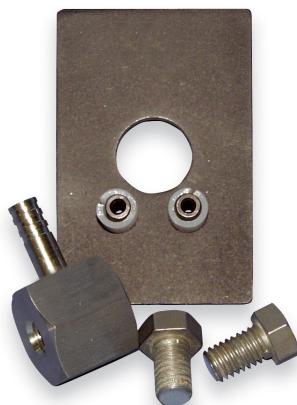


Figure 3.55: A simple pellet press with cell holder. (Cole-Parmer)

Some pellet presses also have a vacuum barb such as the one seen in (Figure 3.55). If your pellet press has one of these, consider using it as it will help remove air from the salt pellet as it is pressed. This ensures a more uniform pellet and removes absorbances in the collected spectrum due to air trapped in the pellet.

3.3.1.5 Preparation of solution cells

Solution cells (Figure 3.56) are a handy way of acquiring infrared spectra of compounds in solution and is particularly handy for monitoring reactions.



Figure 3.56: A sealed solution cell with two injection ports and a schematic of its construction (Perkin-Elmer Inc.)

A thin-film cell consists of two salt plates with a very thin space in between them (Figure 3.57). Two channels allow liquid to be injected and then subsequently removed. The windows on these cells can be made from a variety of IR optical materials. One particularly useful one for water-based solutions is CaF_2 as it is not soluble in water.

Demountable Cell Diagram

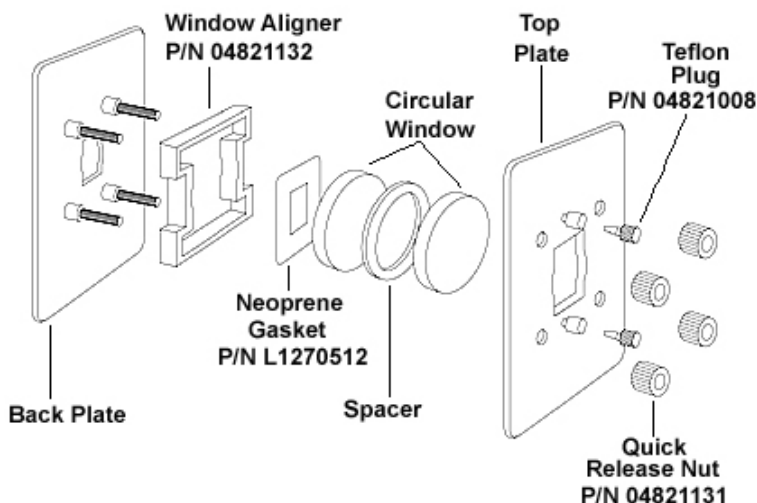


Figure 3.57: A sealed solution cell with two injection ports and a schematic of its construction (Perkin-Elmer Inc.).

Cleaning these cells can be performed by removing the solution, flushing with fresh solvent and gently removing the solvent by syringe. Do not blow air or nitrogen through the ports as this can cause mechanical deformation in the salt window if the pressure is high enough.

3.3.1.6 Deuterated solvent effects

One of the other aspects to solution-phase IR is that the solvent utilized in the cell has a characteristic absorption spectra. In some cases this can be alleviated by replacing the solvent with its deuterated sibling. The benefit here is that C-H bonds are now C-D bonds and have lower vibrational frequencies. Compiled in Figure 3.58 is a set of common solvents.

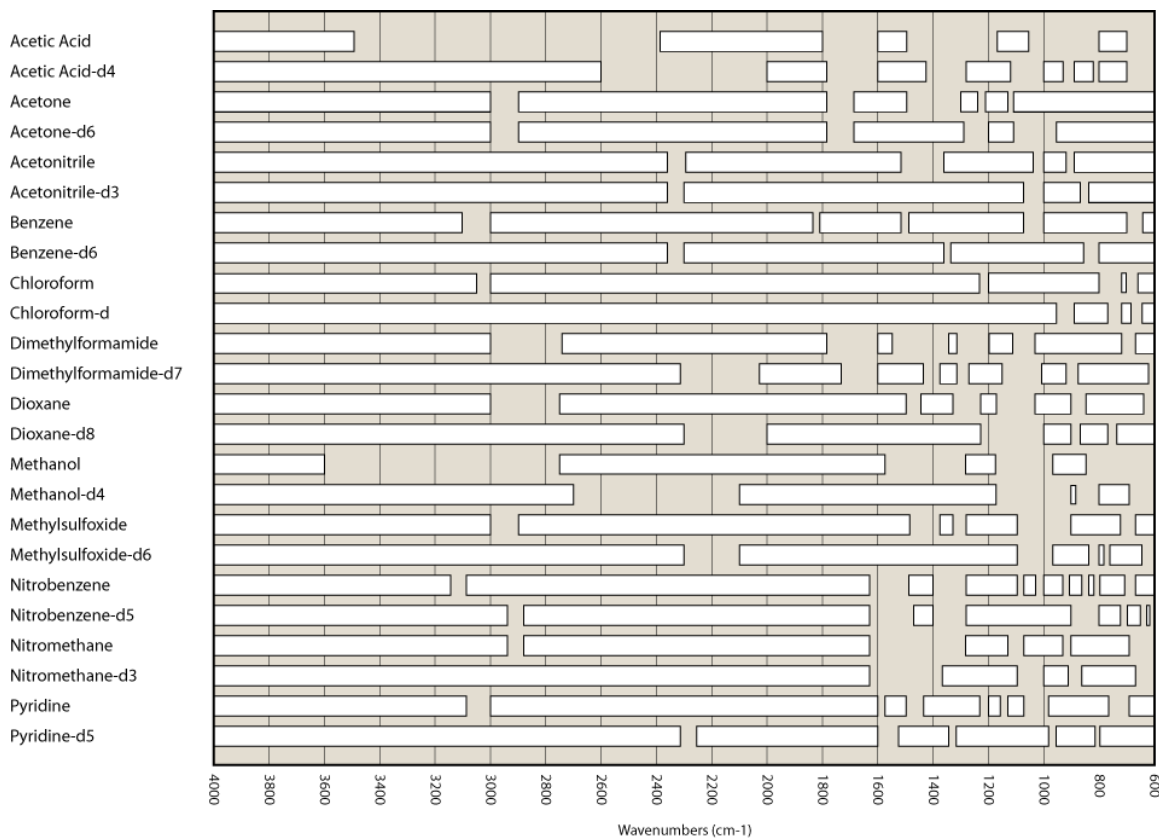


Figure 3.58: IR transparencies of various solvents and their heavy counterparts. Adapted from N. L. McNiven and R. Court, *Appl. Spectrosc.*, 1970, **24**, 296.

This effect has numerous benefits and is often applied to determining what vibrations correspond to what bond in a given molecular sample. This is often accomplished by using isotopically labeled “heavy” reagents such as ones that contain ^2H , ^{15}N , ^{18}O , or ^{13}C .

3.3.1.7 Basic troubleshooting

There are numerous problems that can arise from improperly prepared samples, this section will go through some of the common problems and how to correct them. For this demonstration, spectra of ferrocene will be used. The molecular structure and a photograph of the brightly colored organometallic compound are shown in Figure 3.59 and Figure 3.60.

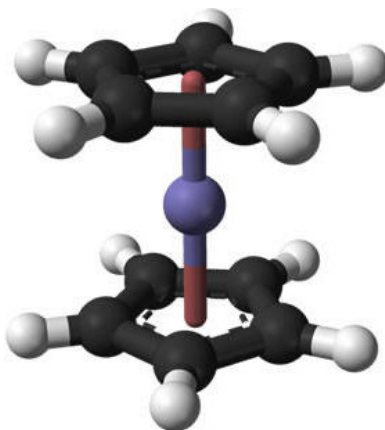


Figure 3.59: Structure of ferrocene ($\text{Fe}(\text{C}_5\text{H}_5)_2$).



Figure 3.60: Image of ferrocene powder ($\text{Fe}(\text{C}_5\text{H}_5)_2$).

Figure 3.61 illustrates what a good sample of ferrocene looks like prepared in a KBr pellet. The peaks are well defined and sharp. No peak is flattened at 0% transmittance and Christiansen scattering is not evident in the baseline.

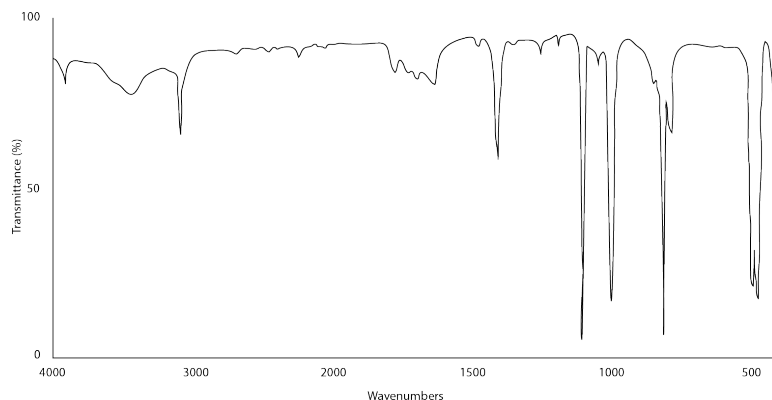


Figure 3.61: A good spectrum of ferrocene in a KBr Pellet. Adapted from NIST Chemistry WebBook.

Figure 3.62 illustrates a sample with some peaks with intensities that are saturated and lose resolution making peak-picking difficult. In order to correct for this problem, scrape some of the sample off of the salt plate with a rubber spatula and reseal the opposite plate. By applying a thinner layer of sample one can improve the resolution of strongly absorbing vibrations.

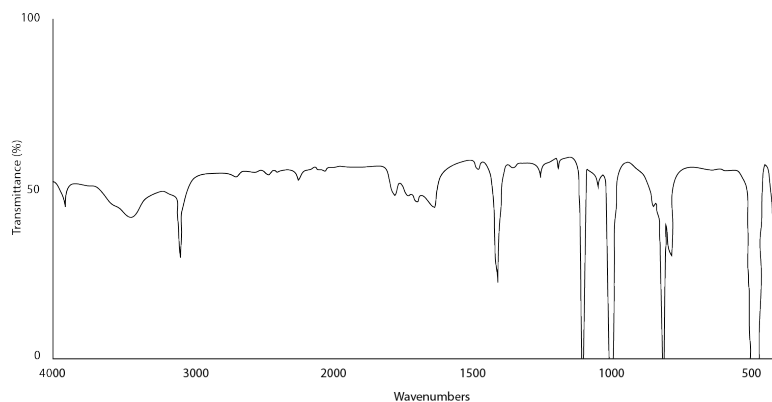


Figure 3.62: An overly concentrated sample of ferrocene in a KBr pellet. Adapted from NIST Chemistry WebBook.

Figure 3.63 illustrates a sample in which too much mineral oil was added to the mull so that the C-H bonds are far more intense than the actual sample. This can be remedied by removing the sample from the plate, grinding more sample and adding a smaller amount of the mull to the plate. Another possible way of doing this is if the sample is insoluble in hexanes, add a little to the mull and wick away the hexane-oil

mixture to leave a dry solid sample. Apply a small portion of oil and replate.

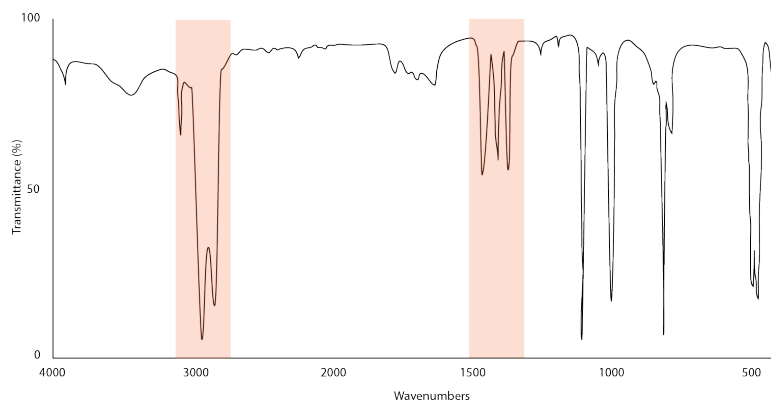


Figure 3.63: A spectrum illustrating the problems of using Nujol, areas highlighted in orange are absorbances related to the addition of Nujol to a sample. Notice how in the 1500 wavenumber region the addition of the Nujol has partially occulted the absorbance by the ferrocene. Adapted from NIST Chemistry WebBook.

Figure 3.64 illustrates the result of particles being too large and scattering light. To remedy this, remove the mull and grind further or else use the solvent deposition technique described earlier.

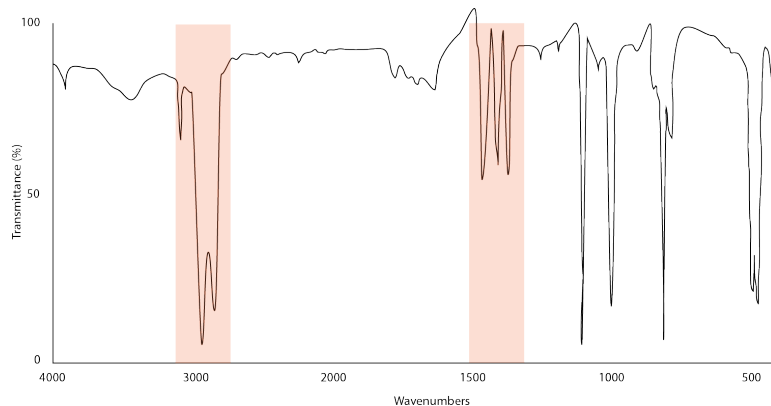


Figure 3.64: A sample exhibiting the Christiansen effect on ferrocene in a Nujol mull. Orange boxes indicate Nujol occult ranges. Adapted from NIST Chemistry WebBook.

3.3.1.8 Bibliography

- N. L. McNiven and R. Court, *Appl. Spectrosc.*, 1970, **24**, 296.

- M. R. Derrick, D. Stulik, and J. M. Landry, in *Scientific Tools in Conservation: Infrared Spectroscopy in Conservation Science*. Getty Conservation Institute, Los Angeles (1999).
- D. L. Pavia, G. M. Lampman, and G. S. Kriz, in *Introduction to Spectroscopy: A Guide for Students of Organic Chemistry*. Harcourt Brace College Publishers, Fort Worth (1996).

3.3.2 Characteristic IR Vibrational Modes for Hydrocarbon Compounds⁸

Functional group	Mode	Wavenumber range (cm ⁻¹)
CH ₃	Asymmetric stretch	2962±10
CH ₃	Symmetric stretch	2872±10
CH ₃	Asymmetric bend	1460±10
CH ₃	Symmetric bend (umbrella mode)	1375±10
CH ₂	Asymmetric stretch	2926±10
CH ₂	Symmetric stretch	2855±10
CH ₂	Scissors	1455±10
CH ₂	Rock	720±10
CH	Stretch	~2900 (weak)
CH	Bend	~1350 (weak)

Table 3.2: Stretching and bending bands for alkanes.

Substitution	C-H stretch (cm ⁻¹)	C=C stretch (cm ⁻¹)	Out of plane bend (cm ⁻¹)
Vinyl	3090 – 3075	1660 - 1630	990±5, 910±5
Vinylidene	3090 – 3075	1660 - 1630	890±5
<i>Cis</i>	3050 – 3000	1660 - 1630	690±10
<i>Trans</i>	3050 – 3000	1680 - 1665	965±5
Tri-substituted	3050 – 3000	1680 - 1665	815±25
Tetra-substituted	-	1680 - 1665	-

Table 3.3: The stretching bands for alkenes.

Substitution	C-H stretch (cm ⁻¹)	C≡C stretch (cm ⁻¹)	C-H wag (cm ⁻¹)
Mono-substituted	3350 – 3250	2140 – 2100	700 - 600
Di-substituted	-	2260 - 2190	-

Table 3.4: The stretching bands for alkynes.

⁸This content is available online at <<http://cnx.org/content/m34623/1.1/>>.

Substitution	Out-of-plane C-H bending (cm^{-1})	Ring bend (cm^{-1})
Mono	770 – 710	690 $\pm$ 10
Ortho	810 - 750	-
Meta	770 - 735	690 $\pm$ 10
Para	860 – 790	-

Table 3.5: Bands for mono- and di-substituted benzene rings.

Vibration	Wavenumber (cm^{-1})
CH ₃ symmetric stretch	2925 $\pm$ 5
CH ₃ bend overtone	2865 $\pm$ 5

Table 3.6: Bands for methyl groups bonded to benzene rings.

3.3.3 Fourier Transform Infrared Spectroscopy of Metal Ligand Complexes⁹

3.3.3.1 Introduction

The infrared (IR) range of the electromagnetic spectrum is usually divided into three regions:

- The far-infrared is always used for rotational spectroscopy, with wavenumber range 400 – 10 cm^{-1} and lower energy.
- The mid-infrared is suitable for a detection of the fundamental vibrations and associated rotational-vibrational structure with the frequency range approximately 4000 – 400 cm^{-1} .
- The near-Infrared with higher energy and wave number range 14000 – 4000 cm^{-1} , can excite overtone or higher harmonic vibrations.

For classical light material interaction theory, if a molecule can interact with an electromagnetic field and absorb a photon of certain frequency, the transient dipole of molecular functional group must oscillate at that frequency. Correspondingly, this transition dipole moment must be a non-zero value, however, some special vibration can be IR inactive for the stretching motion of a homonuclear diatomic molecule and vibrations do not affect the molecule's dipole moment (e.g., N₂).

3.3.3.2 Mechanistic description of the vibrations of polyatomic molecules

A molecule can vibrate in many ways, and each way is called a "vibrational mode". If a molecule has N atoms, linear molecules have 3N-5 degrees of vibrational modes whereas nonlinear molecules have 3N-6 degrees of vibrational modes. Take H₂O for example; a single molecule of H₂O has O-H bending mode (Figure 3.65a), antisymmetric stretching mode (Figure 3.65b), and symmetric stretching mode (Figure 3.65c).

⁹This content is available online at <<http://cnx.org/content/m34660/1.1/>>.

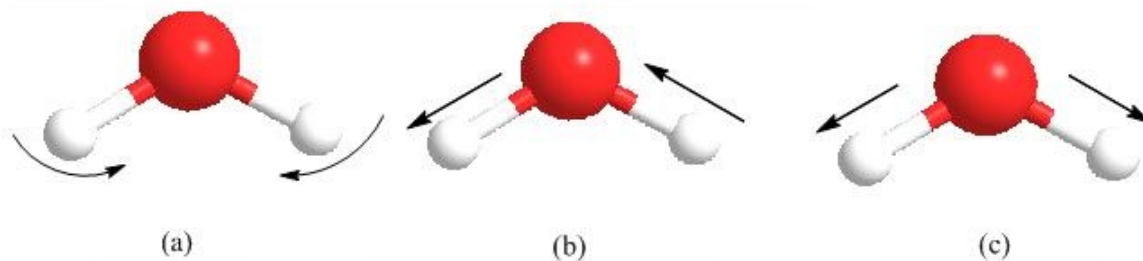


Figure 3.65: Three types of hydroxy vibration modes. (a) bending mode; (b) antisymmetric stretching mode; (c) symmetric stretching mode.

If a diatomic molecule has a harmonic vibration with the energy, (3.1), where $n + \frac{1}{2}$ with $n = 0, 1, 2 \dots$. The motion of the atoms can be determined by the force equation, (3.2), where k is the force constant). The vibration frequency can be described by (3.3). In which m is actually the reduced mass (m_{red} or μ), which is determined from the mass m_1 and m_2 of the two atoms, (3.4).

$$E_n = -h\nu \quad (3.1)$$

$$F = -kx \quad (3.2)$$

$$\omega = (k/m)^{1/2} \quad (3.3)$$

$$m_{\text{red}} = \mu = \frac{m_1 m_2}{m_1 + m_2} \quad (3.4)$$

3.3.3.3 Principle of absorption bands

In IR spectrum, absorption information is generally presented in the form of both wavenumber and absorption intensity or percent transmittance. The spectrum is generally showing wavenumber (cm^{-1}) as the x-axis and absorption intensity or percent transmittance as the y-axis.

Transmittance, "T", is the ratio of radiant power transmitted by the sample (I) to the radiant power incident on the sample (I_0). Absorbance (A) is the logarithm to the base 10 of the reciprocal of the transmittance (T). The absorption intensity of molecule vibration can be determined by the Lambert-Beer Law, (3.5). In this equation, the transmittance spectra ranges from 0 to 100%, and it can provide clear contrast between intensities of strong and weak bands. Absorbance ranges from infinity to zero. The absorption of molecules can be determined by several components. In the absorption equation, ϵ is called molar extinction coefficient, which is related to the molecule behavior itself, mainly the transition dipole moment, c is the concentration of the sample, and l is the sample length. Line width can be determined by the interaction with surroundings.

$$A = \log(I/I_0) = -\log(I/I_0) = \epsilon c l \quad (3.5)$$

3.3.3.4 The infrared spectrometer

As shown in Figure 3.66, there are mainly four parts for fourier transform infrared spectrometer (FTIR):

- **Light source.** Infrared energy is emitted from a glowing black-body source as continuous radiations.
- **Interferometer.** It contains the interferometer, the beam splitter, the fixed mirror and the moving mirror. The beam splitter takes the incoming infrared beam and divides it into two optical beams. One beam reflects off the fixed mirror. The other beam reflects off of the moving mirror which moves a very short distance. After the divided beams are reflected from the two mirrors, they meet each other again at the beam splitter. Therefore, an interference pattern is generated by the changes in the relative position of the moving mirror to the fixed mirror. The resulting beam then passes through the sample and is eventually focused on the detector.
- **Sample compartment.** It is the place where the beam is transmitted through the sample. In the sample compartment, specific frequencies of energy are absorbed.
- **Detector.** The beam finally passes to the detector for final measurement. The two most popular detectors for a FTIR spectrometer are deuterated triglycine sulfate (pyroelectric detector) and mercury cadmium telluride (photon or quantum detector). The measured signal is sent to the computer where the Fourier transformation takes place.

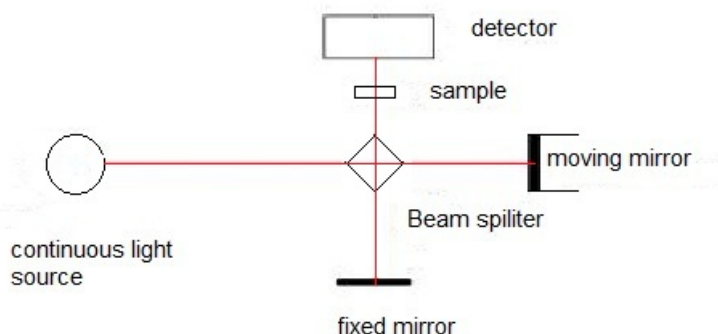


Figure 3.66: The main components of a fourier transform infrared (FTIR) spectrometer.

3.3.3.5 A typical application: the detection of metal ligand complexes

3.3.3.5.1 Some general absorption peaks for common types of functional groups

It is well known that all molecules chemicals have distinct absorption regions in the IR spectrum. Table 3.7 shows the absorption frequencies of common types of functional groups. For systematic evaluation, the IR spectrum is commonly divided into some sub-regions.

- In the region of $4000 - 2000 \text{ cm}^{-1}$, the appearance of absorption bands usually comes from stretching vibrations between hydrogen and other atoms. The O-H and N-H stretching frequencies range from $3700 - 3000 \text{ cm}^{-1}$. If hydrogen bond forms between O-H and other group, it generally caused peak line shape broadening and shifting to lower frequencies. The C-H stretching bands occur in the region of

3300 - 2800 cm^{-1} . The acetylenic C-H exhibits strong absorption at around 3300 cm^{-1} . Alkene and aromatic C-H stretch vibrations absorb at 3200-3000 cm^{-1} . Generally, asymmetric vibrational stretch frequency of alkene C-H is around 3150 cm^{-1} , and symmetric vibrational stretch frequency is between 3100 cm^{-1} and 3000 cm^{-1} . The saturated aliphatic C-H stretching bands range from 3000 - 2850 cm^{-1} , with absorption intensities that are proportional to the number of C-H bonds. Aldehydes often show two sharp C-H stretching absorption bands at 2900 - 2700 cm^{-1} . However, in water solution, C-H vibrational stretch is much lower than in non-polar solution. It means that the strong polarity solution can greatly reduce the transition dipole moment of C-H vibration.

- Furthermore, the stretching vibrations frequencies between hydrogen and other heteroatoms are between 2600 - 2000 cm^{-1} , for example, S-H at 2600 - 2550 cm^{-1} , P-H at 2440 - 2275 cm^{-1} , Si-H at 2250 - 2100 cm^{-1} .
- The absorption bands at the 2300 - 1850 cm^{-1} region usually present only from triple bonds, such as $\text{C}\equiv\text{C}$ at 2260 - 2100 cm^{-1} , $\text{C}\equiv\text{N}$ at 2260 - 2000 cm^{-1} , diazonium salts $-\text{N}\equiv\text{N}$ at approximately 2260 cm^{-1} , allenes $\text{C}=\text{C}=\text{C}$ at 2000 - 1900 cm^{-1} . The peaks of these groups are all have strong absorption intensities. The 1950 - 1450 cm^{-1} region stands for double-bonded functional groups vibrational stretching.
- Most carbonyl $\text{C}=\text{O}$ stretching bands range from 1870 - 1550 cm^{-1} , and the peak intensities are from mean to strong. Conjugation, ring size, hydrogen bonding, and steric and electronic effects can lead to significant shifts in absorption frequencies. Furthermore, if carbonyl links with electron-withdrawing group, such as acid chlorides and acid anhydrides, it would give rise to IR bands at 1850 - 1750 cm^{-1} . Ketones usually display stretching bands at 1715 cm^{-1} .
- None conjugated aliphatic $\text{C}=\text{C}$ and $\text{C}=\text{N}$ have absorption bands at 1690 - 1620 cm^{-1} . Besides, around 1430 and 1370 cm^{-1} , there are two identical peaks presenting C-H bending.
- The region from 1300 - 910 cm^{-1} always includes the contributions from skeleton C-O and C-C vibrational stretches, giving additional molecular structural information correlated with higher frequency areas. For example, ethyl acetate not only shows its carbonyl stretch at 1750 - 1735 cm^{-1} , but also exhibits its identical absorption peaks at 1300 - 1000 cm^{-1} from the skeleton vibration of C-O and C-C stretches.

Group	Frequency (cm^{-1})	Strength appearance
C-H stretch	2850 - 3400	Strong in nonpolar solvent Weak in polar solvent
O-H stretch N-H stretch	3200 - 3700	Broad in solvent
$\text{C}\equiv\text{N}$ stretch R-N=C=S stretch	2050 - 2300	Medium or strong
$\text{C}\equiv\text{O}$ stretch (bound with metal)	around 2000	Medium or strong
$\text{C}\equiv\text{C}$ stretch	2100 - 2260	Weak
$\text{C}=\text{O}$ stretch	ca 1715 (ketone), ca 1650 (amides)	Strong
$\text{C}=\text{C}$ stretch	1450 - 1700	Weak to strong
<i>continued on next page</i>		

C-H bend	1260 - 1470	Strong
C-O stretch	1040 - 1300	Medium or strong

Table 3.7: The typical frequencies of functional groups.

3.3.3.5.2 General introduction of metal ligand complex

The metal electrons fill into the molecular orbital of ligands (CN, CO, etc.) to form complex compound. As shown in Figure 3.67, a simple molecular orbital diagram for CO can be used to explain the binding mechanism.

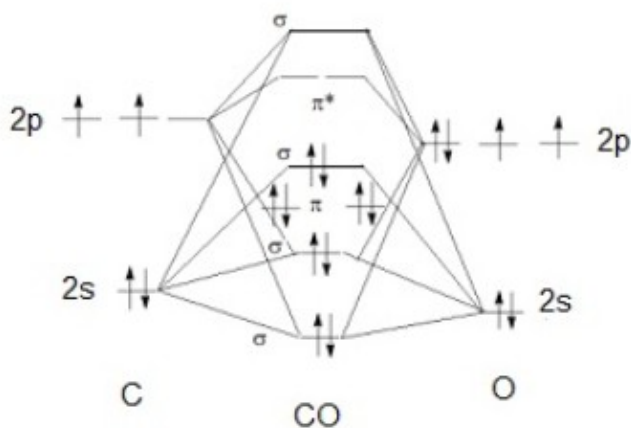


Figure 3.67: Molecular orbital diagram for carbon monoxide (CO).

The CO and metal can bind with three ways:

- Donation of a pair of electrons from the C-O σ^* orbital into an empty metal orbital (Figure 3.68a).
- Donation from a metal d orbital into the C-O π^* orbital to form a M-to-CO π -back bond (Figure 3.68b).
- Under some conditions a pair of carbon π electron can donate into an empty metal d-orbital.

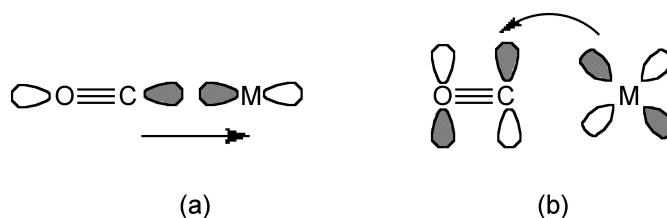


Figure 3.68: Main binding interaction types between metal and CO. (a) CO-to-metal σ bond; (b) M-to-CO π -back bond.

3.3.3.5.3 Some factors to influence the band shifts and strength

Herein, we mainly consider two properties: ligand stretch frequency and their absorption intensity. Take the ligand CO for example again. The frequency shift of the carbonyl peaks in the IR mainly depends on the bonding mode of the CO (terminal or bridging) and electron density on the metal. The intensity and peak numbers of the carbonyl bands depends on some factors: CO ligands numbers, geometry of the metal ligand complex and fermi resonance.

3.3.3.5.3.1 Effect on electron density on metal

As shown in Table 3.8, a greater charge on the metal center result in the CO stretches vibration frequency decreasing. For example, $[\text{Ag}(\text{CO})]^+$ show higher frequency of CO than free CO, which indicates a strengthening of the CO bond. σ donation removes electron density from the nonbonding HOMO of CO. From Figure 3.67, it is clear that the HOMO has a small amount of anti-bonding property, so removal of an electron actually increases (slightly) the CO bond strength. Therefore, the effect of charge and electronegativity depends on the amount of metal to CO π -back bonding and the CO IR stretching frequency.

d^x	Complex	νCO stretch frequency (cm^{-1})
	free CO	2143
d^{10}	$[\text{Ag}(\text{CO})]^+$	2204
d^{10}	$\text{Ni}(\text{CO})_4$	2060
d^{10}	$[\text{Co}(\text{CO})_4]^-$	1890
d^6	$[\text{Mn}(\text{CO})_6]^+$	2090
d^6	$\text{Cr}(\text{CO})_6$	2000
d^6	$[\text{V}(\text{CO})_6]^-$	1860

Table 3.8: Different types of ligands frequencies of different electron density on a metal center.

If the electron density on a metal center is increasing, more π -back bonding to the CO ligand(s) will also increase, as shown in Table 3.8. It means more electron density would enter into the empty carbonyl π^* orbital and weaken the C-O bond. Therefore, it makes the M-CO bond strength increasing and more double-bond-like ($\text{M}=\text{C}=\text{O}$).

3.3.3.5.3.2 Ligand donation effect

Some cases, as shown in Table 3.9, different ligands would bind with same metal at the same metal-ligand complex. For example, if different electron density groups bind with $\text{Mo}(\text{CO})_3$ as the same form, as shown in Figure 3.69, the CO vibrational frequencies would depend on the ligand donation effect. Compared with the PPh_3 group, CO stretching frequency which the complex binds the PF_3 group (2090, 2055 cm^{-1}) is higher. It indicates that the absolute amount of electron density on that metal may have certain effect on the ability of the ligands on a metal to donate electron density to the metal center. Hence, it may be explained by the Ligand donation effect. Ligands that are *trans* to a carbonyl can have a large effect on the ability of the CO ligand to effectively π -backbond to the metal. For example, two *trans* π -backbonding ligands will partially compete for the same d-orbital electron density, weakening each other's net M-L π -backbonding. If the *trans* ligand is a π -donating ligand, the free metal to CO π -backbonding can increase the M-CO bond strength (more $\text{M}=\text{C}=\text{O}$ character). It is well known that pyridine and amines are not those strong π -donors. However, they are even worse π -backbonding ligands. So the CO is actually easy for π -back donation without any competition. Therefore, it naturally reduces the CO IR stretching frequencies in metal carbonyl complexes for the ligand donation effect.

Metal Ligand Complex	CO stretch frequency (cm^{-1})
$\text{Mo}(\text{CO})_3(\text{PF}_3)_3$	2090, 2055
$\text{Mo}(\text{CO})_3[\text{P}(\text{OMe})_3]_3$	1977, 1888
$\text{Mo}(\text{CO})_3(\text{PPh}_3)_3$	1934, 1835
$\text{Mo}(\text{CO})_3(\text{NCCH}_3)_3$	1915, 1783
$\text{Mo}(\text{CO})_3(\text{pyridine})_3$	1888, 1746

Table 3.9: The effect of different types of ligands on the frequency of the carbonyl ligand.

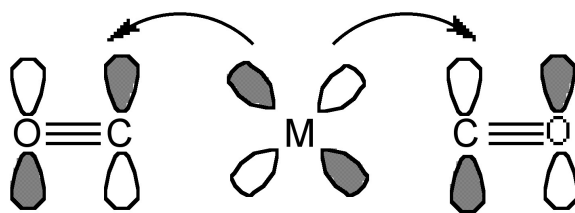


Figure 3.69: Schematic representation of competitive back-donation from a transition metal to multiple π -acceptor ligands

3.3.3.5.3.3 Geometry effects

Some cases, metal-ligand complex can form not only terminal but also bridging geometry. As shown in Figure 3.70, in the compound $\text{Fe}_2(\text{CO})_7(\text{dipy})$, CO can act as a bridging ligand. Evidence for a bridging mode of coordination can be easily obtained through IR spectroscopy. All the metal atoms bridged by a carbonyl can donate electron density into the π^* orbital of the CO and weaken the CO bond, lowering vibration frequency of CO. In this example, the CO frequency in terminal is around 2080 cm^{-1} , and in bridge, it shifts to around 1850 cm^{-1} .

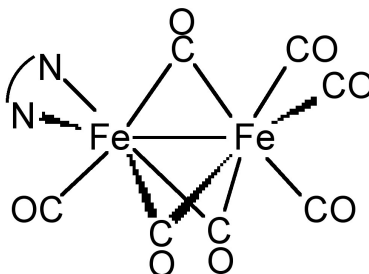


Figure 3.70: The structure of $\text{Fe}_2(\text{CO})_7(\text{dipy})$.

3.3.3.6 Bibliography

- *Introduction of Fourier Transform Infrared Spectrometry*, Thermo Nicolet Corporation (2001).
- C. P. S. Hsu, *Handbook of Instrumental Techniques for Analytical Chemistry*. Prentice-Hall, NJ (1997).
- B. E. Douglas, D. H. McDaniel, and J. J. Alexander, *Concepts and Models of Inorganic Chemistry*, 3rd Ed., John Wiley & Sons, Winchester (1994).
- A. F. Cotton and M. J. Troup, *J. Am. Chem. Soc.*, 1974, **96**, 1233.
- K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed., Wiley, New York (1978).

3.3.4 Pump-probe Detection of Molecular Functional Group Vibrational Lifetime¹⁰

3.3.4.1 Introduction

The dynamics of molecular functional group plays an important role during a chemical process, chemical bond forming and breaking, energy transfer and other dynamics happens within picoseconds domain. It is very difficult to study such fast processes directly, for decades scientists can only learn from theoretical calculations, lacking experimental methods.

However, with the development of ultrashort pulsed laser enable experimental study of molecular functional group dynamics. With ultrafast laser technologies, people develop a series of measuring methods, among which, pump-probe technique is widely used to study the molecular functional group dynamics. Here we concentrate on how to use pump-probe experiment to measure functional group vibrational lifetime. The principle, experimental setup and data analysis will be introduced.

3.3.4.2 Principles of the pump-probe technique

For every function group within a molecule, such as the $\text{C}\equiv\text{N}$ triple bond in phenyl selenocyanate ($\text{C}_6\text{H}_5\text{SeCN}$) or the C-D single bond in deuterated chloroform (DCCl_3), they have an individual infrared vibrational mode and associated energy levels. For a typical 3-level system (Figure 3.71), both the 0 to 1 and the 1 to 2 transition are near the probe pulse frequency (they don't necessarily need to have exactly the same frequency).

¹⁰This content is available online at <<http://cnx.org/content/m34610/1.2/>>.

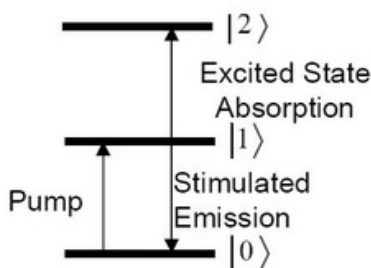


Figure 3.71: Schematic representation of a typical three level system.

In a pump-probe experiment, we use the geometry as is shown in Figure 3.72. Two synchronized laser beams, one of which is called pump beam (E_{pu}) while the other probe beam (E_{pr}). There is a delay in time between each pulse. The laser pulses hit the sample, the intensity of ultrafast laser (fs or ps) is strong enough to generate 3rd order polarization and produce 3rd order optical response signal which is used to give dynamics information of molecular function groups. For the total response signals we have (3.6), where μ_{10} , μ_{21} are transition dipole moment and E_0 , E_1 , and E_2 are the energies of the three levels, and t_3 is the time delay between pump and probe beam. The delay t_3 is varied and the response signal intensity is measured. The functional group vibration life time is determined from the data.

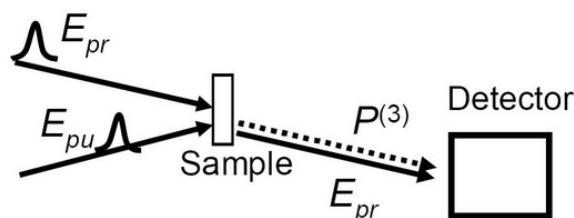
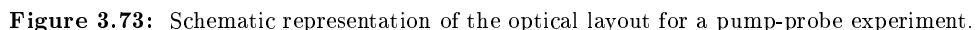


Figure 3.72: The geometry of the pump-probe experiment.

$$S = 4\mu_{10}^4 e^{-i(E_1-E_0)t_3/\hbar - \Gamma t_3} - 2\mu_{10}^2 \mu_{21}^2 e^{-i(E_1-E_0)t_3/\hbar - \Gamma t_3} \quad (3.6)$$

3.3.4.3 Typical experimental set-up

The optical layout of a typical pump-probe setup is schematically displayed in Figure 3.73. In the setup, the output of the oscillator (500 mW at 77 MHz repetition rate, 40 nm bandwidth centered at 800 nm) is split into two beams (1:4 power ratio). Of this, 20% of the power is to seed a femtosecond (fs) amplifier whose output is 40 fs pulses centered at 800 nm with power of ~ 3.4 W at 1 KHz repetition rate. The rest (80%) of the seed goes through a bandpass filter centered at 797.5 nm with a width of 0.40 nm to seed a picosecond (ps) amplifier. The power of the stretched seed before entering the ps amplifier cavity is only ~ 3 mW. The



In a typical pump-probe setup, the ps IR beam is collimated and used as the pump beam. Approximately 1% of the fs IR OPA output is used as the probe beam whose intensity is further modified by a polarizer placed before the sample. Another polarizer is placed after the sample and before the spectrograph to select different polarizations of the signal. The signal is then sent into a spectrograph to resolve frequency, and detected with a mercury cadmium telluride (MCT) dual array detector. Use of a pump pulse (femtosecond, wide band) and a probe pulse (picoseconds, narrow band), scanning the delay time and reading the data from the spectrometer, will give the lifetime of the functional group. The wide band pump and spectrometer described here is for collecting multiple group of pump-probe combination.

For a typical pump-probe curve shown in Figure 3.74 life time t is defined as the corresponding time value to the half intensity as time zero.

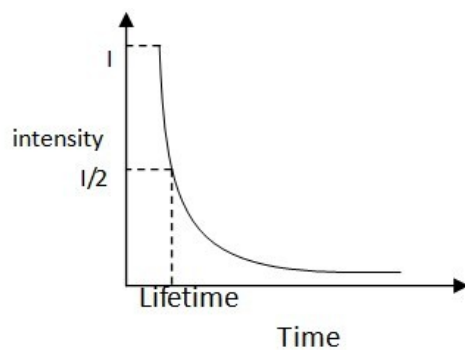


Figure 3.74: A typical pump-probe curve.

Table 3.10 shows the pump-probe data of the $\text{C}\equiv\text{N}$ triple bond in a series of aromatic cyano compounds: *n*-propyl cyanide ($\text{C}_3\text{H}_7\text{CN}$), ethyl thiocyanate ($\text{C}_2\text{H}_5\text{SCN}$), and ethyl selenocyanate ($\text{C}_2\text{H}_5\text{SeCN}$) for which the $\nu_{\text{C}\equiv\text{N}}$ for each compound (measured in CCl_4 solution) is 2252 cm^{-1} , 2156 cm^{-1} , and $\sim 2155\text{ cm}^{-1}$, respectively.

Delay (ps)	$\text{C}_3\text{H}_7\text{CN}$	$\text{C}_2\text{H}_5\text{SCN}$	$\text{C}_2\text{H}_5\text{SeCN}$
0	-0.00695	-0.10918	-0.06901
0.1	-0.0074	-0.10797	-0.07093
0.2	-0.00761	-0.1071	-0.07247
0.3	-0.00768	-0.10545	-0.07346
0.4	-0.0076	-0.10487	-0.07429
0.5	-0.00778	-0.10287	-0.07282
0.6	-0.00782	-0.10286	-0.07235
0.7	-0.00803	-0.10222	-0.07089
0.8	-0.00764	-0.10182	-0.07073
0.9	-0.00776	-0.10143	-0.06861
1	-0.00781	-0.10099	-0.06867
1.1	-0.00745	-0.10013	-0.06796
<i>continued on next page</i>			

1.2	-0.00702	-0.10066	-0.06773
1.3	-0.00703	-0.0989	-0.06767
1.4	-0.00676	-0.0995	-0.06638
1.5	-0.00681	-0.09757	-0.06691
1.6	-0.00639	-0.09758	-0.06696
1.7	-0.00644	-0.09717	-0.06583
1.8	-0.00619	-0.09741	-0.06598
1.9	-0.00613	-0.09723	-0.06507
2	-0.0066	-0.0962	-0.06477
2.5	-0.00574	-0.09546	-0.0639
3	-0.0052	-0.09453	-0.06382
3.5	-0.00482	-0.09353	-0.06389
4	-0.0042	-0.09294	-0.06287
4.5	-0.00387	-0.09224	-0.06197
5	-0.00351	-0.09009	-0.06189
5.5	-0.00362	-0.09084	-0.06188
6	-0.00352	-0.08938	-0.06021
6.5	-0.00269	-0.08843	-0.06028
7	-0.00225	-0.08788	-0.05961
7.5	-0.00231	-0.08694	-0.06065
8	-0.00206	-0.08598	-0.05963
8.5	-0.00233	-0.08552	-0.05993
9	-0.00177	-0.08503	-0.05902
9.5	-0.00186	-0.08508	-0.05878
10	-0.00167	-0.0842	-0.0591
11	-0.00143	-0.08295	-0.05734

Table 3.10: Pump-probe intensity data for C $\equiv$ N stretching frequency in *n*-propyl cyanide, ethyl thiocyanate, and ethyl selenocyanate as a function of delay (ps).

A plot of intensity versus time for the data from TABLE is shown Figure 3.75. From these curves the C $\equiv$ N stretch lifetimes can be determined for C₃H₇CN, C₂H₅SCN, and C₂H₅SeCN as ~ 5.5 ps, ~ 84 ps, and ~ 282 ps, respectively.

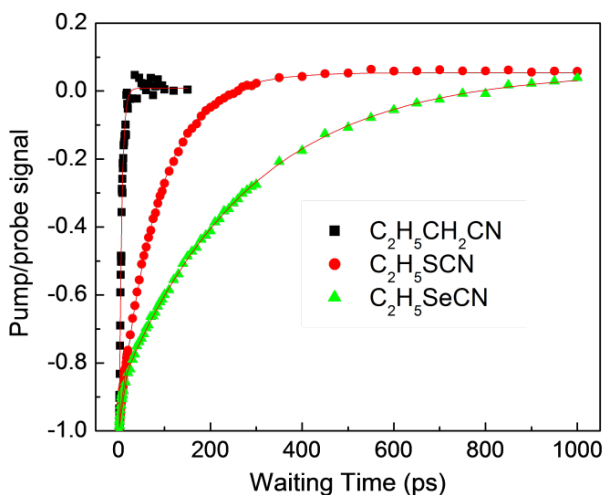


Figure 3.75: The $C\equiv N$ stretch lifetimes for benzyl cyanide, phenyl thiocyanate, and phenyl selenocyanate.

From what is shown above, the pump-probe method is used in detecting $C\equiv N$ vibrational lifetimes in different chemicals. One measurement only takes several second to get all the data and the lifetime, showing that pump-probe method is a powerful way to measure functional group vibrational lifetime.

3.4 UV-Visible Spectroscopy

3.4.1 Basics of UV-Visible Spectroscopy¹¹

3.4.1.1 Introduction

Ultraviolet-visible (UV-vis) spectroscopy is used to obtain the absorbance spectra of a compound in solution or as a solid. What is actually being observed spectroscopically is the absorbance of light energy or electromagnetic radiation, which excites electrons from the ground state to the first singlet excited state of the compound or material. The UV-vis region of energy for the electromagnetic spectrum covers 1.5 - 6.2 eV which relates to a wavelength range of 800 - 200 nm. The Beer-Lambert Law, (3.7), is the principle behind absorbance spectroscopy. For a single wavelength, A is absorbance (unitless, usually seen as arb. units or arbitrary units), ϵ is the molar absorptivity of the compound or molecule in solution ($M^{-1}cm^{-1}$), b is the path length of the cuvette or sample holder (usually 1 cm), and c is the concentration of the solution (M).

$$A = \epsilon bc \quad (3.7)$$

There are three types of absorbance instruments used to collect UV-vis spectra:

- 1) Single beam spectrometer.
- 2) Double beam spectrometer.

¹¹This content is available online at <<http://cnx.org/content/m34525/1.1/>>.

3) Simultaneous spectrometer.

All of these instruments have a light source (usually a deuterium or tungsten lamp), a sample holder and a detector, but some have a filter for selecting one wavelength at a time. The single beam instrument (Figure 3.76) has a filter or a monochromator between the source and the sample to analyze one wavelength at a time. The double beam instrument (Figure 3.77) has a single source and a monochromator and then there is a splitter and a series of mirrors to get the beam to a reference sample and the sample to be analyzed, this allows for more accurate readings. In contrast, the simultaneous instrument (Figure 3.78) does not have a monochromator between the sample and the source; instead, it has a diode array detector that allows the instrument to simultaneously detect the absorbance at all wavelengths. The simultaneous instrument is usually much faster and more efficient, but all of these types of spectrometers work well.

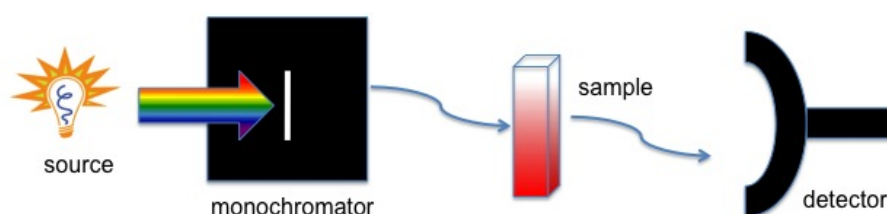


Figure 3.76: Illustration of a single beam UV-vis instrument.

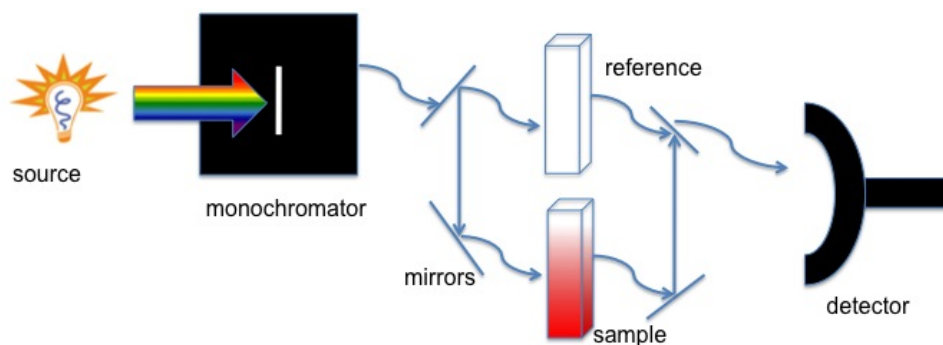


Figure 3.77: Illustration of a double beam UV-vis instrument.

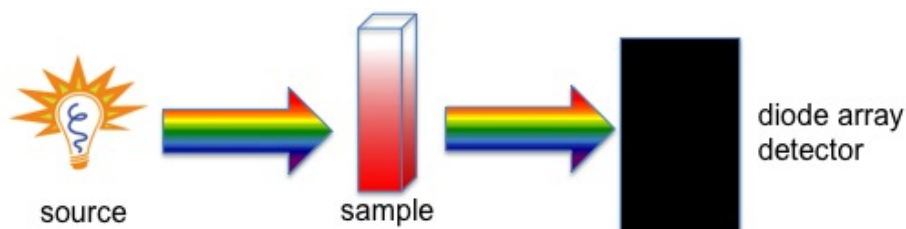


Figure 3.78: Illustration of a simultaneous UV-vis instrument.

3.4.1.2 What information can be obtained from UV-vis spectra?

UV-vis spectroscopic data can give qualitative and quantitative information of a given compound or molecule. Irrespective of whether quantitative or qualitative information is required it is important to use a reference cell to zero the instrument for the solvent the compound is in. For quantitative information on the compound, calibrating the instrument using known concentrations of the compound in question in a solution with the same solvent as the unknown sample would be required. If the information needed is just proof that a compound is in the sample being analyzed, a calibration curve will not be necessary; however, if a degradation study or reaction is being performed, and concentration of the compound in solution is required, thus a calibration curve is needed.

To make a calibration curve, at least three concentrations of the compound will be needed, but five concentrations would be most ideal for a more accurate curve. The concentrations should start at just above the estimated concentration of the unknown sample and should go down to about an order of magnitude lower than the highest concentration. The calibration solutions should be spaced relatively equally apart, and they should be made as accurately as possible using digital pipettes and volumetric flasks instead of graduated cylinders and beakers. An example of absorbance spectra of calibration solutions of Rose Bengal (4,5,6,7-tetrachloro-2',4',5',7'-tetraiodofluorescein, Figure 3.79) can be seen in Figure 3.80. To make a calibration curve, the value for the absorbances of each of the spectral curves at the highest absorbing wavelength, is plotted in a graph similar to that in Figure 3.81 of absorbance versus concentration. The correlation coefficient of an acceptable calibration is 0.9 or better. If the correlation coefficient is lower than that, try making the solutions again as the problem may be human error. However, if after making the solutions a few times the calibration is still poor, something may be wrong with the instrument; for example, the lamps may be going bad.

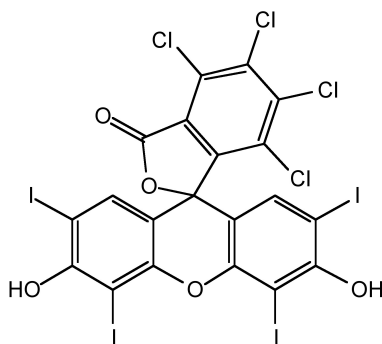


Figure 3.79: The molecular structure of Rose Bengal (4,5,6,7-tetrachloro-2',4',5',7'-tetraiodofluorescein).

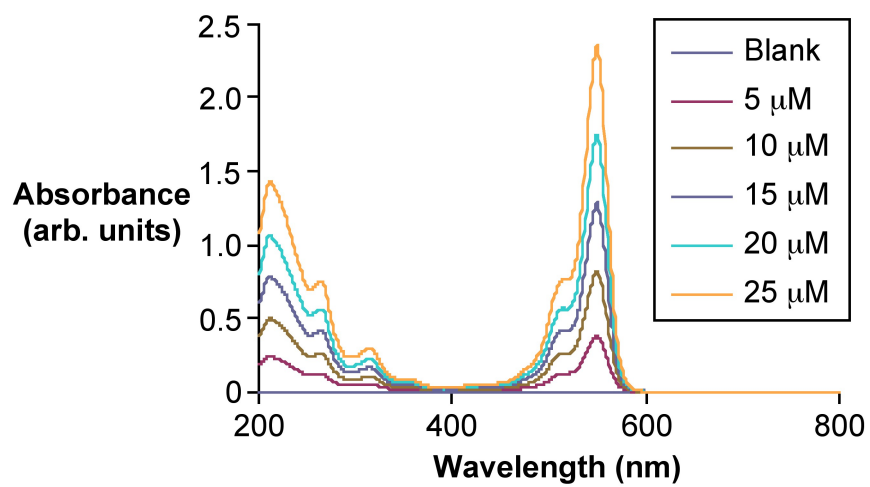


Figure 3.80: UV-vis spectra of different concentrations of Rose Bengal.

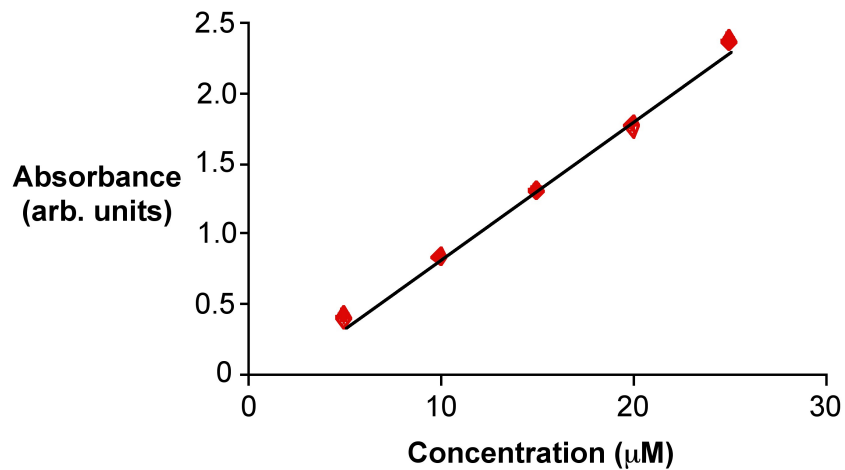


Figure 3.81: Calibration curve of Rose Bengal. Equation of line: $y = 0.0977x - 0.1492$ ($R^2 = 0.996$)

3.4.1.3 Limitations of UV-visible spectroscopy

3.4.1.3.1 Sample

UV-vis spectroscopy works well on liquids and solutions, but if the sample is more of a suspension of solid particles in liquid, the sample will scatter the light more than absorb the light and the data will be very skewed. Most UV-vis instruments can analyze solid samples or suspensions with a diffraction apparatus (Figure 3.82), but this is not common. UV-vis instruments generally analyze liquids and solutions most efficiently.

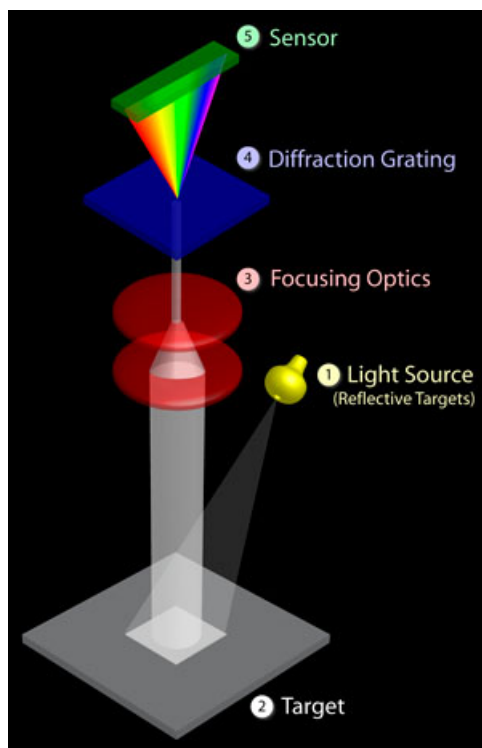


Figure 3.82: Schematic representation of the apparatus for collecting UV-vis spectra from solid materials.

3.4.1.3.2 Calibration and reference

A blank reference will be needed at the very beginning of the analysis of the solvent to be used (water, hexanes, etc), and if concentration analysis needs to be performed, calibration solutions need to be made accurately (e.g., Figure 3.81). If the solutions are not made accurately enough, the actual concentration of the sample in question will not be accurately determined.

3.4.1.3.3 Choice of solvent or container

Every solvent has a UV-vis absorbance cutoff wavelength. The solvent cutoff is the wavelength below which the solvent itself absorbs all of the light. So when choosing a solvent be aware of its absorbance cutoff and where the compound under investigation is thought to absorb. If they are close, chose a different solvent. Table 3.11 provides an example of solvent cutoffs.

Solvent	UV absorbance cutoff (nm)
Acetone	329
Benzene	278
Dimethylformamide (DMF)	267
Ethanol	205
Toluene	285
Water	180

Table 3.11: UV absorbance cutoffs of various common solvents.

The material the cuvette (the sample holder) is made from will also have a UV-vis absorbance cutoff. Glass will absorb all of the light higher in energy starting at about 300 nm, so if the sample absorbs in the UV, a quartz cuvette will be more practical as the absorbance cutoff is around 160 nm for quartz (Table 3.12).

Material	Wavelength range (nm)
Glass	380 - 780
Plastic	380 - 780
Fused quartz	below 380

Table 3.12: Three different types of cuvettes commonly used, with different usable wavelengths.

3.4.1.3.4 Concentration of solution

To obtain reliable data, the peak of absorbance of a given compound needs to be at least three times higher in intensity than the background noise of the instrument. Obviously using higher concentrations of the compound in solution can combat this. Also, if the sample is very small and diluting it would not give an acceptable signal, there are cuvettes that hold smaller sample sizes than the 2.5 mL of a standard cuvettes. Some cuvettes are made to hold only 100 μ L, which would allow for a small sample to be analyzed without having to dilute it to a larger volume, lowering the signal to noise ratio.

3.4.1.4 Bibliography

- D. A. Skoog, F. J. Holler, S. R. Crouch, *Principles of Instrumental Analysis*, 6th Ed., Thomson Brooks/Cole (2007).
- J. P. Sibilio, *Materials Characterization and Chemical Analysis*, 2nd Ed., Wiley-VCH, New York (1996).
- D. C. Harris, *Quantitative Chemical Analysis*, 7th Ed., Freeman, New York(2007).

3.5 Photoluminescence and Fluorescence Spectroscopy

3.5.1 Photoluminescence Spectroscopy and its Applications¹²

3.5.1.1 Introduction

3.5.1.1.1 What is photoluminescence

Photoluminescence spectroscopy is a contactless, nondestructive method of probing the electronic structure of materials. Light is directed onto a sample, where it is absorbed and imparts excess energy into the material in a process called *photo-excitation*. One way this excess energy can be dissipated by the sample is through the emission of light, or *luminescence*. In the case of photo-excitation, this luminescence is called *photoluminescence*.

Photo-excitation causes electrons within a material to move into permissible excited states. When these electrons return to their equilibrium states, the excess energy is released and may include the emission of light (a radiative process) or may not (a nonradiative process). The energy of the emitted light (photoluminescence) relates to the difference in energy levels between the two electron states involved in the transition between the excited state and the equilibrium state. The quantity of the emitted light is related to the relative contribution of the radiative process.

3.5.1.1.2 The importance of photoluminescence

In most photoluminescent systems chromophore aggregation generally quenches light emission via aggregation-caused quenching (ACQ). This means that it is necessary to use and study fluorophores in dilute solutions or as isolated molecules. This in turn results in poor sensitivity of devices employing fluorescence, e.g., biosensors and bioassays. However, there have recently been examples reported in which luminogen aggregation played a constructive, instead of destructive role in the light-emitting process. This aggregated-induced emission (AIE) is of great potential significance in particular with regard to solid state devices. Photoluminescence spectroscopy provides a good method for the study of luminescent properties of a fluorophore.

3.5.1.1.3 Forms of photoluminescence

3.5.1.1.3.1 Resonant radiation

In resonant radiation, a photon of a particular wavelength is absorbed and an equivalent photon is immediately emitted, through which no significant internal energy transitions of the chemical substrate between absorption and emission are involved and the process is usually of an order of 10 nanoseconds.

3.5.1.1.3.2 Fluorescence

When the chemical substrate undergoes internal energy transitions before relaxing to its ground state by emitting photons, some of the absorbed energy is dissipated so that the emitted light photons are of lower energy than those absorbed. One of such most familiar phenomenon is fluorescence, which has a short lifetime (10^{-8} to 10^{-4} s).

3.5.1.1.3.3 Phosphorescence

Phosphorescence is a radiational transition, in which the absorbed energy undergoes intersystem crossing into a state with a different spin multiplicity. The lifetime of phosphorescence is usually from 10^{-4} - 10^{-2} s, much longer than that of Fluorescence. Therefore, phosphorescence is even rarer than fluorescence, since a molecule in the triplet state has a good chance of undergoing intersystem crossing to ground state before phosphorescence can occur.

¹²This content is available online at <<http://cnx.org/content/m38357/1.2/>>.

3.5.1.1.4 Relation between absorption and emission spectra

Fluorescence and phosphorescence come at lower energy than absorption (the excitation energy). As shown in Figure 3.83, in absorption, wavelength λ_0 corresponds to a transition from the ground vibrational level of S_0 to the lowest vibrational level of S_1 . After absorption, the vibrationally excited S_1 molecule relaxes back to the lowest vibrational level of S_1 prior to emitting any radiation. The highest energy transition comes at wavelength λ_0 , with a series of peaks following at longer wavelength. The absorption and emission spectra will have an approximate mirror image relation if the spacings between vibrational levels are roughly equal and if the transition probabilities are similar. The λ_0 transitions in Figure 3.84 do not exactly overlap. As shown in Figure 3.83, a molecule absorbing radiation is initially in its electronic ground state, S_0 . This molecule possesses a certain geometry and solvation. As the electronic transition is faster than the vibrational motion of atoms or the translational motion of solvent molecules, when radiation is first absorbed, the excited S_1 molecule still possesses its S_0 geometry and solvation. Shortly after excitation, the geometry and solvation change to their most favorable values for S_1 state. This rearrangement lowers the energy of excited molecule. When an S_1 molecule fluoresces, it returns to the S_0 state with S_1 geometry and solvation. This unstable configuration must have a higher energy than that of an S_0 molecule with S_0 geometry and solvation. The net effect in Figure 3.83 is that the λ_0 emission energy is less than the λ_0 excitation energy.

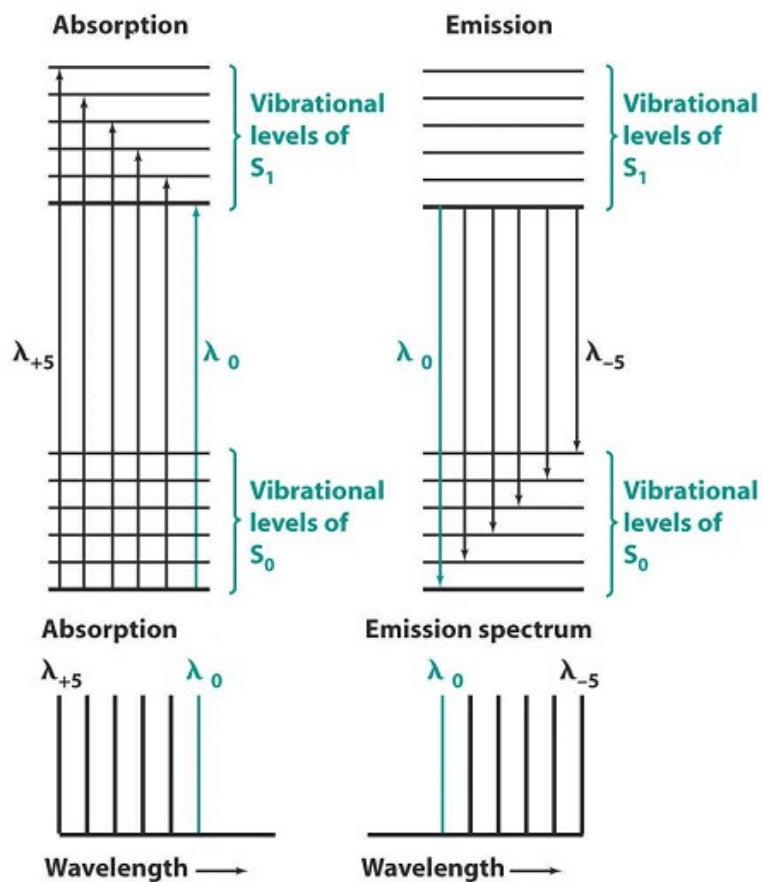


Figure 3.83: Energy-level diagram showing why structure is seen in the absorption and emission spectra and why the spectra are roughly mirror images of each other. Adapted from D. C. Harris, *Quantitative Chemical Analysis*, 7th Ed, W. H. Freeman and Company, New York (2006).

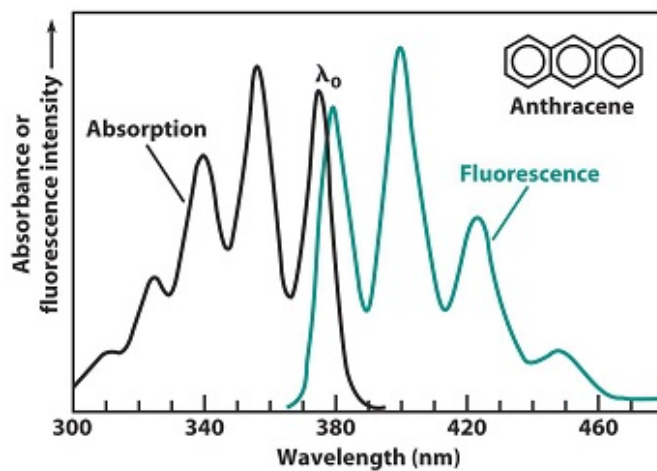


Figure 3.84: Excitation and emission spectra of anthracene that have the same mirror image relation at the absorption and emission spectra. Adapted from C. M. Byron and T. C. Werner, *J. Chem. Ed.*, 1991, **68**, 433.

3.5.1.2 Instrumentation

A schematic of an emission experiment is given in Figure 3.85. An excitation wavelength is selected by one monochromator, and luminescence is observed through a second monochromator, usually positioned at 90° to the incident light to minimize the intensity of scattered light reaching the detector. If the excitation wavelength is fixed and the emitted radiation is scanned, an emission spectrum is produced.

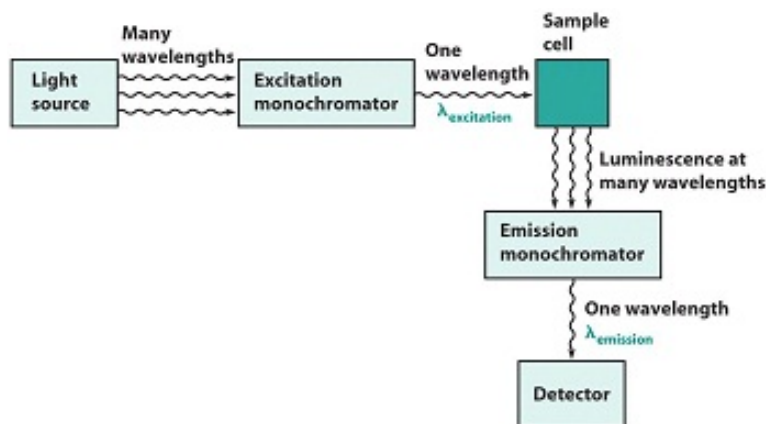


Figure 3.85: Essentials of a luminescence experiment. The sample is irradiated at one wavelength and emission is observed over a range of wavelengths. The excitation monochromator selects the excitation wavelength and the emission monochromator selects one wavelength at a time to observe. Adapted from D. C. Harris, *Quantitative Chemical Analysis*, 7th Edition, W. H. Freeman and Company, New York, (2006).

3.5.1.3 Relationship to UV-visible spectroscopy

Ultraviolet-visible (UV-vis) spectroscopy or ultraviolet-visible spectrophotometry refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. The absorption or reflectance in the visible range directly affects the perceived color of the chemicals involved. In the UV-vis spectrum, an absorbance versus wavelength graph results and it measures transitions from the ground state to excited state, while photoluminescence deals with transitions from the excited state to the ground state.

An excitation spectrum is a graph of emission intensity versus excitation wavelength. An excitation spectrum looks very much like an absorption spectrum. The greater the absorbance is at the excitation wavelength, the more molecules are promoted to the excited state and the more emission will be observed.

By running an UV-vis absorption spectrum, the wavelength at which the molecule absorbs energy most and is excited to a large extent can be obtained. Using such value as the excitation wavelength can thus provide a more intense emission at a red-shifted wavelength, which is usually within twice of the excitation wavelength.

3.5.1.4 Applications

3.5.1.4.1 Detection of ACQ or AIE properties

Aggregation-caused quenching (ACQ) of light emission is a general phenomenon for many aromatic compounds that fluorescence is weakened with an increase in its solution concentration and even condensed phase. Such effect, however, comes into play in the solid state, which has prevented many lead luminogens identified by the laboratory solution-screening process from finding real-world applications in an engineering robust form.

Aggregation-induced emission (AIE), on the other hand, is a novel phenomenon that aggregation plays a constructive, instead of destructive role in the light-emitting process, which is exactly opposite to the ACQ effect.

3.5.1.4.1.1 A case study

From the photoluminescence spectra of hexaphenylsilole (HPS, Figure 3.86) shown in Figure 3.87, it can be seen that as the water (bad solvent) fraction increases, the emission intensity of HPS increases. For BODIPY derivative (Figure 3.88) in Figure 3.89, it shows that the PL intensity peaks at 0 water content resulted from intramolecular rotation or twisting, known as *twisted intramolecular charge transfer* (TICT).

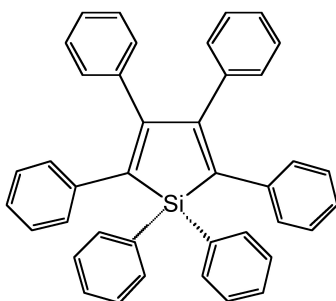


Figure 3.86: The structure of hexaphenylsilole (HPS).

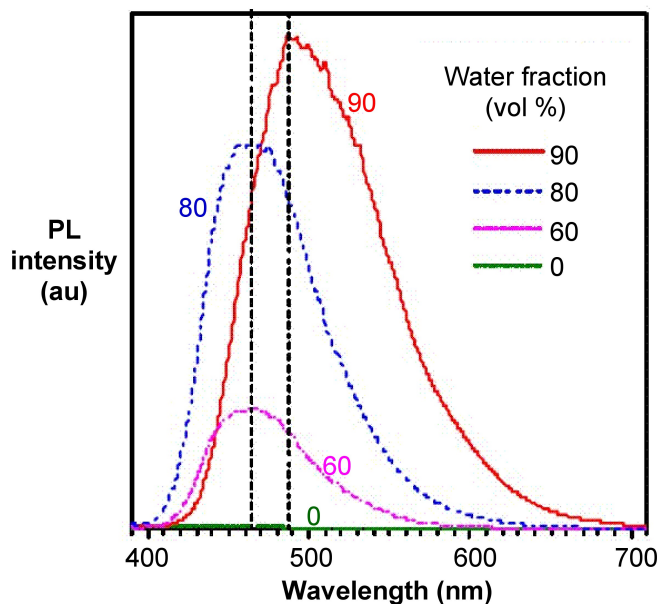


Figure 3.87: PL spectra of HPS solutions in acetonitrile/water mixtures. Adapted from Y. Hong, J. W. Y. Lam, and B. Z. Tang, *Chem. Commun.*, 2009, 4332. Copyright: The Royal Society of Chemistry (2009).

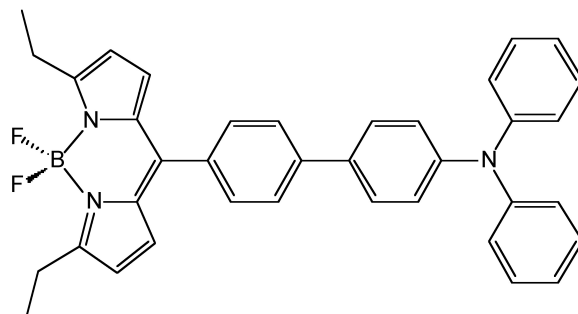


Figure 3.88: The structure of a triphenylamine–boradiazaindacene (BODIPY) derivative.

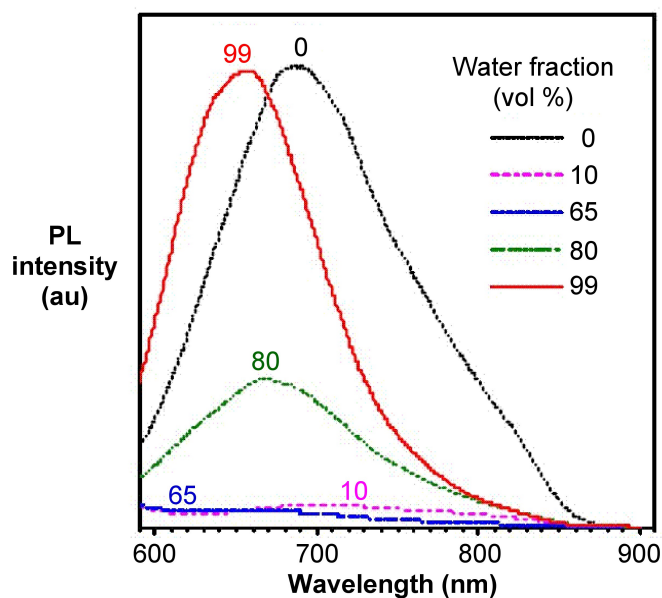


Figure 3.89: PL spectra of BODIPY derivative in THF/water mixtures. Adapted from Y. Hong, J. W. Y. Lam, and B. Z. Tang, *Chem. Commun.*, 2009, 4332. Copyright: The Royal Society of Chemistry (2009).

The emission color of an AIE luminogen is scarcely affected by solvent polarity, whereas that of a TICT luminogen typically bathochromically shifts with increasing solvent polarity. In Figure 3.90, however, it shows different patterns of emission under different excitation wavelengths. At the excitation wavelength of 372 nm, which is corresponding to the BODIPY group, the emission intensity increases as water fraction increases. However, it decreases at the excitation wavelength of 530 nm, which is corresponding to the TPE group. The presence of two emissions in this compound is due to the presence of two independent groups in

the compound with AIE and ACQ properties, respectively.

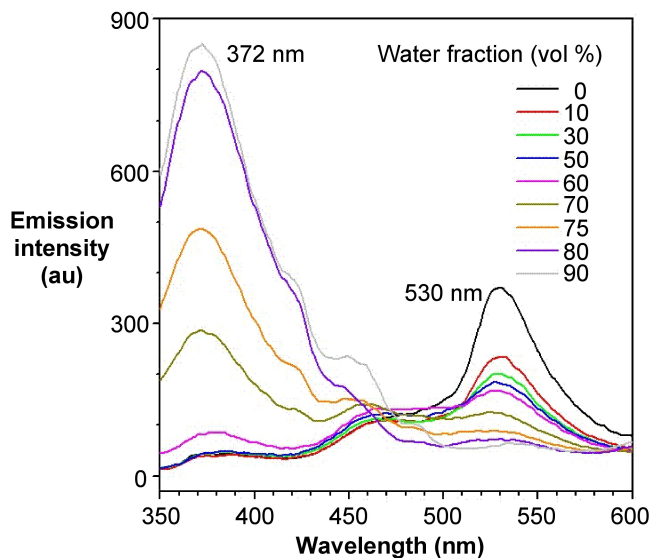


Figure 3.90: PL spectra of compound containing AIE and ACQ groups in THF/water mixtures at the excitation wavelength of 329 nm. Adapted from Y. Hong, J. W. Y. Lam, and B. Z. Tang, *Chem. Commun.*, 2009, 4332. Copyright: The Royal Society of Chemistry (2009).

3.5.1.4.1.2 Detection of luminescence with respect to molarity

Figure 3.91 shows the photoluminescence spectroscopy of a BODIPY-TPE derivative of different concentrations. At the excitation wavelength of 329 nm, as the molarity increases, the emission intensity decreases. Such compounds whose PL emission intensity enhances at low concentration can be a good chemo-sensor for the detection of the presence of compounds with low quantity.

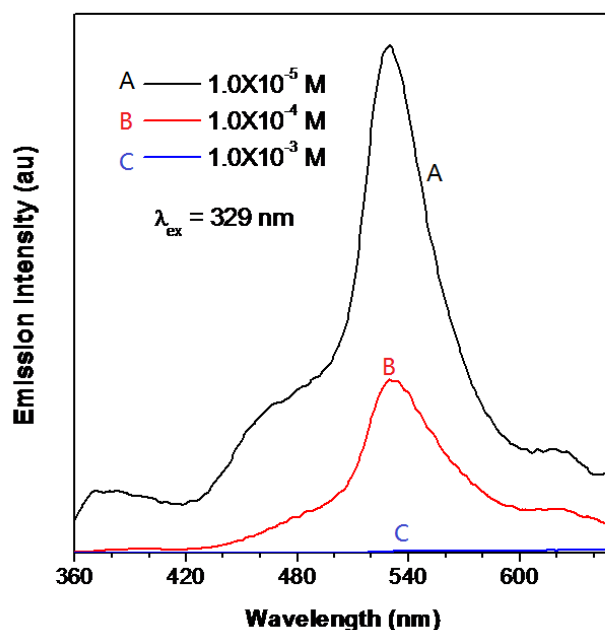


Figure 3.91: PL spectra of a BODIPY derivative solution in different concentrations in THF at excitation wavelength of 329 nm.

3.5.1.4.2 Other applications

Apart from the detection of light emission patterns, photoluminescence spectroscopy is of great significance in other fields of analysis, especially semiconductors.

3.5.1.4.2.1 Band gap determination

Band gap is the energy difference between states in the conduction and valence bands, of the radiative transition in semiconductors. The spectral distribution of PL from a semiconductor can be analyzed to nondestructively determine the electronic band gap. This provides a means to quantify the elemental composition of compound semiconductor and is a vitally important material parameter influencing solar cell device efficiency.

3.5.1.4.2.2 Impurity levels and defect detection

Radiative transitions in semiconductors involve localized defect levels. The photoluminescence energy associated with these levels can be used to identify specific defects, and the amount of photoluminescence can be used to determine their concentration. The PL spectrum at low sample temperatures often reveals spectral peaks associated with impurities contained within the host material. Fourier transform photoluminescence microspectroscopy, which is of high sensitivity, provides the potential to identify extremely low concentrations of intentional and unintentional impurities that can strongly affect material quality and device performance.

3.5.1.4.2.3 Recombination mechanisms

The return to equilibrium, known as “recombination”, can involve both radiative and nonradiative processes. The quantity of PL emitted from a material is directly related to the relative amount of radiative and nonradiative recombination rates. Nonradiative rates are typically associated with impurities and the amount of photoluminescence and its dependence on the level of photo-excitation and temperature are directly related to the dominant recombination process. Thus, analysis of photoluminescence can qualitatively monitor changes in material quality as a function of growth and processing conditions and help understand the underlying physics of the recombination mechanism.

3.5.1.4.2.4 Surface structure and excited states

The widely used conventional methods such as XRD, IR and Raman spectroscopy, are very often not sensitive enough for supported oxide catalysts with low metal oxide concentrations. Photoluminescence, however, is very sensitive to surface effects or adsorbed species of semiconductor particles and thus can be used as a probe of electron-hole surface processes.

3.5.1.5 Limitations of photoluminescence spectroscopy

Very low concentrations of optical centers can be detected using photoluminescence, but it is not generally a quantitative technique. The main scientific limitation of photoluminescence is that many optical centers may have multiple excited states, which are not populated at low temperature.

The disappearance of luminescence signal is another limitation of photoluminescence spectroscopy. For example, in the characterization of photoluminescence centers of silicon no sharp-line photoluminescence from 969 meV centers was observed when they had captured self-interstitials.

3.5.1.6 Bibliography

- Y. Hong, J. W. Y. Lam, and B. Z. Tang, *Chem. Commun.*, 2009, 4332.
- M. Anpo, M. Kondo, S. Coluccia, C. Louis, and M. Che, *J. Am. Chem. Soc.*, 1989, **111**, 8791.
- N. S. Sariciftci, *Primary Photoexcitations In Conjugated Polymers Molecular Exciton Versus Semiconductor Band Model*, World Scientific Publishing Company, Singapore (1997).
- D. C. Harris, *Quantitative Chemical Analysis*, 7th Ed, W. H. Freeman and Company, New York (2006).
- G. Davies, *Phys. Rep.*, 1989, **176**, 83.

3.5.2 Fluorescence Characterization and its Application in DNA Detection¹³

3.5.2.1 Introduction to fluorescence

Luminescence is a process involving the emission of light from any substance, and occurs from electronically excited states of that substance. Normally, luminescence is divided into two categories, *fluorescence* and *phosphorescence*, depending on the nature of the excited state.

NOTE: Fluorescence is the emission of electromagnetic radiation light by a substance that has absorbed radiation of a different wavelength. Phosphorescence is a specific type of photoluminescence related to fluorescence. Unlike fluorescence, a phosphorescent material does not immediately re-emit the radiation it absorbs.

The process of fluorescent absorption and emission is easily illustrated by the Jablonski diagram. A classic Jablonski diagram is shown in Figure 3.92, where S_n represents the n^{th} electronic states. There are different vibrational and rotational states in every electronic state. After light absorption, a fluorophore is excited to a higher electronic and vibrational state from ground state (here rotational states are not considered for

¹³This content is available online at <<http://cnx.org/content/m34680/1.1/>>.

simplicity). By internal conversion of energy, these excited molecules relax to lower vibrational states in S_1 (Figure 3.92) and then return to ground states by emitting fluorescence. Actually, excited molecules always return to higher vibration states in S_0 and followed by some thermal process to ground states in S_1 . It is also possible for some molecules to undergo intersystem crossing process to T_2 states (Figure 3.92). After internal conversion and relaxing to T_1 , these molecules can emit phosphorescence and return to ground states.

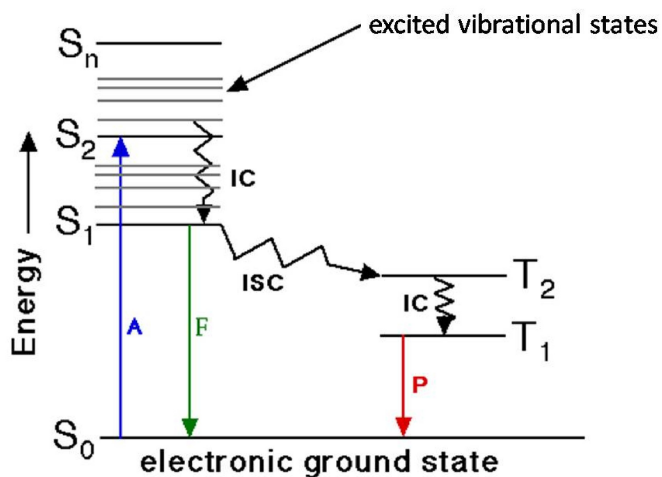


Figure 3.92: Jablonski diagram where, A = absorbance, F = fluorescence, P = phosphorescence, S = single state, T = triplet state, IC = internal conversion, ISC = intersystem crossing.

The Stokes shift, the excited state lifetime and quantum yield are the three most important characteristics of fluorescence emission. Stokes shift is the difference between positions of the band maxima of the absorption and emission spectra of the same electronic transition. According to mechanism discussed above, an emission spectrum must have lower energy or longer wavelength than absorption light. The quantum yield is a measure of the intensity of fluorescence, as defined by the ratio of emitted photons over absorbed photons. Excited state lifetime is a measure of the decay times of the fluorescence.

3.5.2.2 Instrumentation of Fluorescence Spectroscopy

3.5.2.2.1 Spectrofluorometers

Most spectrofluorometers can record both excitation and emission spectra. An emission spectrum is the wavelength distribution of an emission measured at a single constant excitation wavelength. In comparison, an excitation spectrum is measured at a single emission wavelength by scanning the excitation wavelength.

3.5.2.2.2 Light sources

Specific light sources are chosen depending on the application.

3.5.2.2.2.1 Arc and incandescent xenon lamps

The high-pressure xenon (Xe) arc is the most versatile light source for steady-state fluorometers now. It can provides a steady light output from 250 - 700 nm (Figure 3.93), with only some sharp lines near 450 and 800

nm. The reason that xenon arc lamps emit a continuous light is the recombination of electrons with ionized Xe atoms. These ions produced by collision between Xe and electrons. Those sharp lines near 450 nm are due to the excited Xe atoms that are not ionized.

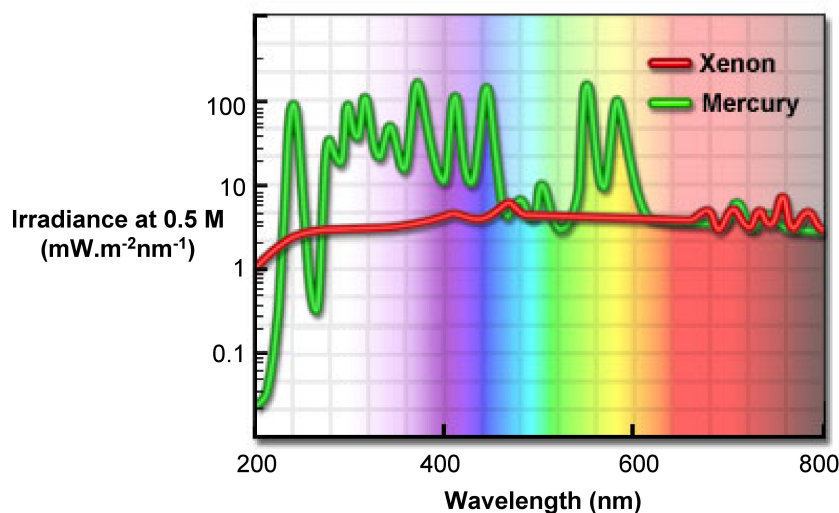


Figure 3.93: Spectral irradiance of arc-discharge lamps.

During fluorescence experiment, some distortion of the excitation spectra can be observed, especially the absorbance locating in visible and ultraviolet region. Any distortion displayed in the peaks is the result of wavelength-dependent output of Xe lamps. Therefore, we need to apply some mathematic and physical approaches for correction.

3.5.2.2.2.2 High-pressure mercury (Hg) lamps

Compared with xenon lamps, Hg lamps have higher intensities. As shown in Figure 3.93, the intensity of Hg lamps is concentrated in a series of lines, so it is a potentially better excitation light source if matched to certain fluorophores.

3.5.2.2.2.3 Xe-Hg arc lamps

High-pressure xenon-mercury lamps have been produced. They have much higher intensity in ultraviolet region than normal Xe lamps. Also, the introduction of Xe to Hg lamps broadens the sharp-line output of Hg lamps. Although the wavelength of output is still dominated by those Hg lines, these lines are broadened and fit to various fluorophores better. The Xe-Hg lamp output depends on the operating temperature.

3.5.2.2.2.4 Low pressure Hg and Hg-Ar lamps

Due to their very sharp line spectra, they are primarily useful for calibration purpose. The combination of Hg and Ar improve the output scale, from 200 - 1000 nm.

3.5.2.2.2.5 Other light source

There are many other light source for experimental and industrial application, such as pulsed xenon lamps, quartz-tungsten halogen (QTH) lamps, LED light sources, etc.

3.5.2.2.3 Monochromators

Most of the light sources used provide only polychromatic or white light. However, what is needed for experiments are various chromatic light with a wavelength range of 10 nm. Monochromators help us to achieve this aim. Prisms and diffraction gratings are the two main kinds of monochromators used, although diffraction gratings are most useful, especially in spectrofluorometers.

Dispersion, efficiency, stray light level and resolution are important parameters for monochromators. Dispersion is mainly determined by slit width and expressed in nm/mm. It is prepared to have low stray light level. Stray light is defined as light transmitted by the monochromator at wavelength outside the chosen range. Also, a high efficiency is required to increase the ability to detect low light levels. Resolution depends on the slit width. There are normally two slits, entrance and exit in a fluorometers. Light intensity that passes through the slits is proportional to the square of the slit width. Larger slits have larger signal levels, but lower resolution, and vice versa. Therefore, it is important to balance the signal intensity and resolution with the slit width.

3.5.2.2.4 Optical filters

Optical filters are used in addition to monochromators, because the light passing through monochromator is rarely ideal, optical filters are needed for further purifying light source. If the basic excitation and emission properties of a particular system under study, then selectivity by using optical filters is better than by the use of monochromators. Two kinds of optical filter are gradually employed: colored filters and thin-film filters.

3.5.2.2.4.1 Colored filter

Colored filters are the most traditional filter used before thin-film filter were developed. They can be divided into two categories: monochromatic filter and long-pass filter. The first one only pass a small range of light (about 10 - 25 nm) centered at particular chosen wavelength. In contrast, long pass filter transmit all wavelengths above a particular wavelength. In using these bandpass filters, special attention must be paid to the possibility of emission from the filter itself, because many filters are made up of luminescent materials that are easily excited by UV light. In order to avoid this problem, it is better to set up the filter further away from the sample.

3.5.2.2.4.2 Thin-film filters

The transmission curves of colored class filter are not suitable for some application and as such they are gradually being substituted by thin-film filters. Almost any desired transmission curve can be obtained using a thin film filter.

3.5.2.2.5 Detectors

The standard detector used in many spectrofluorometers is the InGaAs array, which can provides rapid and robust spectral characterization in the near-IR. And the liquid-nitrogen cooling is applied to decrease the background noise. Normally, detectors are connected to a controller that can transfer a digital signal to and from the computer.

3.5.2.3 Fluorophores

At present a wide range of fluorophores have been developed as fluorescence probes in bio-system. They are widely used for clinical diagnosis, bio-tracking and labeling. The advance of fluorometers has been accompanied with developments in fluorophore chemistry. Thousands of fluorophores have been synthesized, but herein four categories of fluorophores will be discussed with regard their spectral properties and application.

3.5.2.3.1 Intrinsic or natural fluorophores

Tryptophan (trp), tyrosine (tyr), and phenylalanine (phe) are three natural amino acid with strong fluorescence (Figure 3.94). In tryptophan, the indole groups absorbs excitation light as UV region and emit fluorescence.

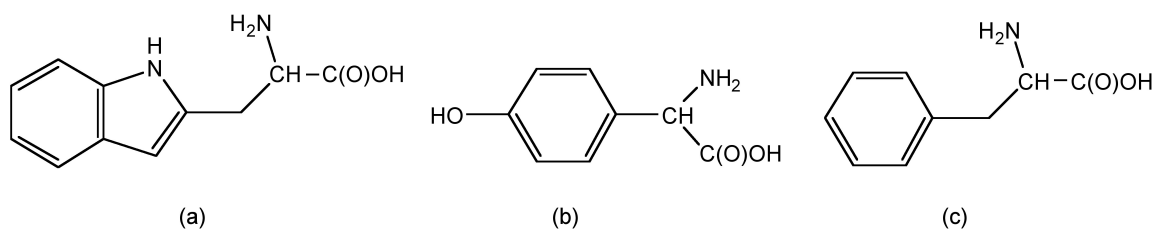


Figure 3.94: The structure of (a) tryptophan, (b) tyrosine and (c) phenylalanine.

Green fluorescent proteins (GFP) is another natural fluorophores. GFP is composed of 238 amino acids (Figure 3.95), and it exhibits a characteristic bright green fluorescence when excited. They are mainly extracted from bioluminescent jellyfish *Aequorea victoria*, and are employed as signal reporters in molecular biology.

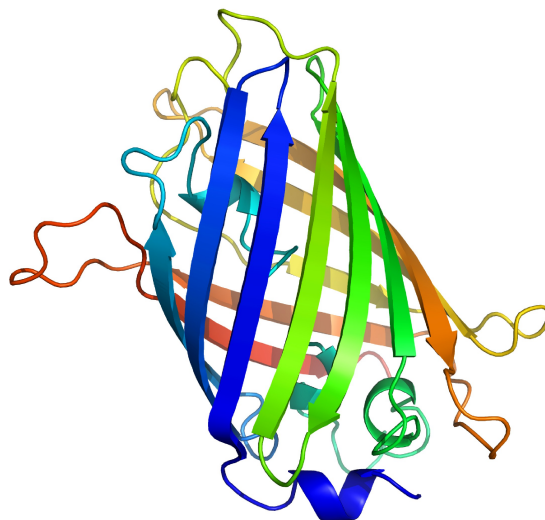


Figure 3.95: Green fluorescent proteins (GFP) ribbon diagram.

3.5.2.3.2 Extrinsic fluorophores

Most bio-molecules are nonfluorescent, therefore it is necessary to connect different fluorophores to enable labeling or tracking of the biomolecules. For example, DNA is an example of a biomolecule without fluorescence. The Rhodamine (Figure 3.96) and BODIPY (Figure 3.97) families are two kinds of well-developed organic fluorophores. They have been extensively employed in design of molecular probes due to their excellent photophysical properties.

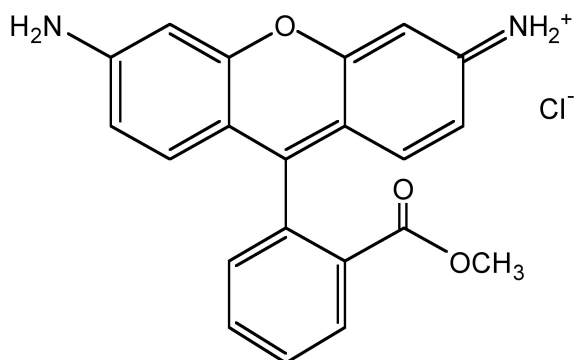


Figure 3.96: The structure of Rhodamine 123.

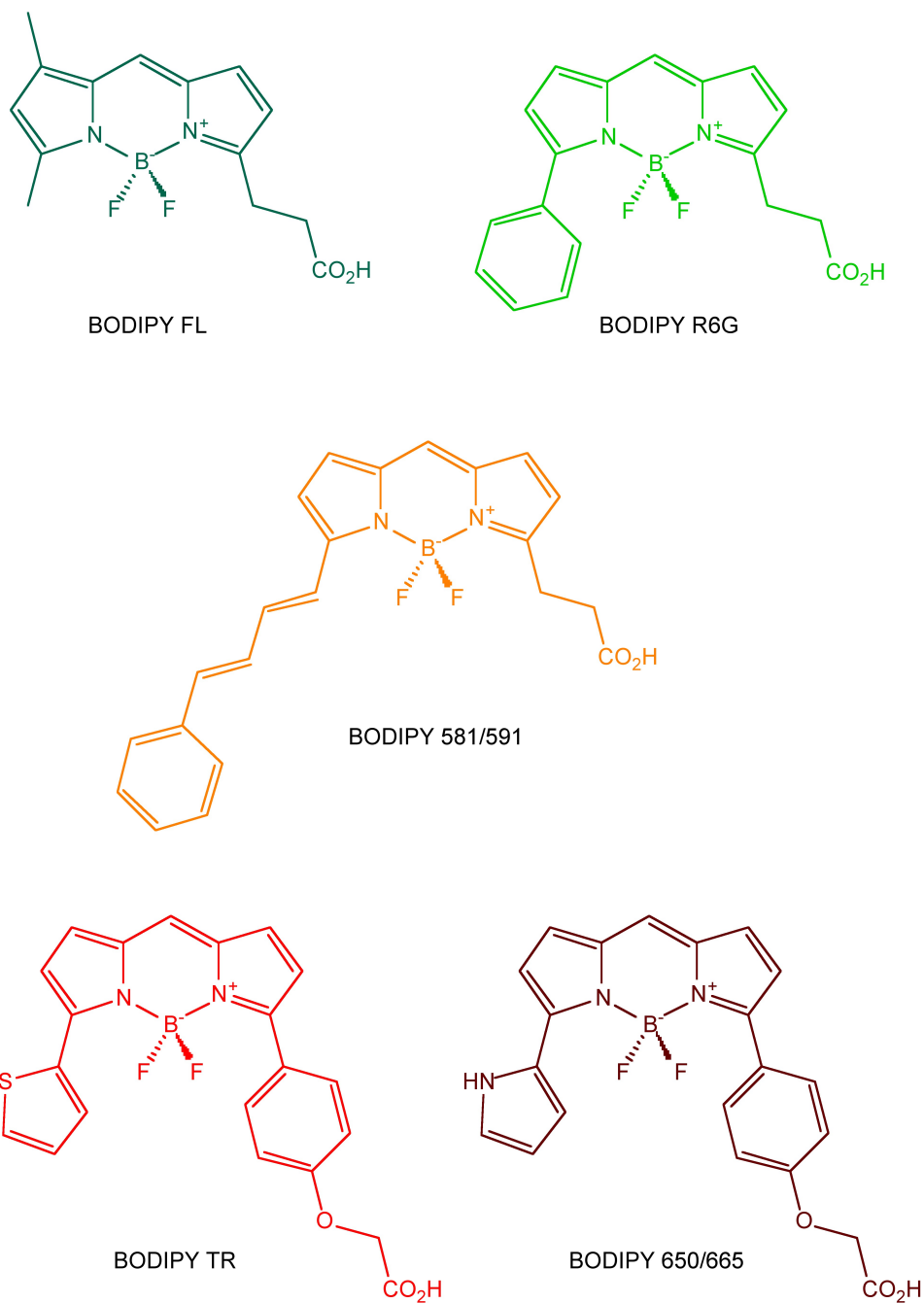


Figure 3.97: The structure of selected boron-dipyrromethane (BODIPY) derivatives with their characteristic emission colors.

3.5.2.3.3 Red and near-infrared (NIR) dyes

With the development of fluorophores, red and near-infrared (NIR) dyes attract increasing attention since they can improve the sensitivity of fluorescence detection. In biological system, autofluorescence always increase the ratio of signal-to-noise (S/N) and limit the sensitivity. As the excitation wavelength turns to longer, autofluorescence decreases accordingly, and therefore signal-to-noise ratio increases. Cyanines are one such group of long-wavelength dyes, e.g., Cy-3, Cy-5 and Cy-7 (Figure 3.98), which have emission at 555, 655 and 755 nm respectively.

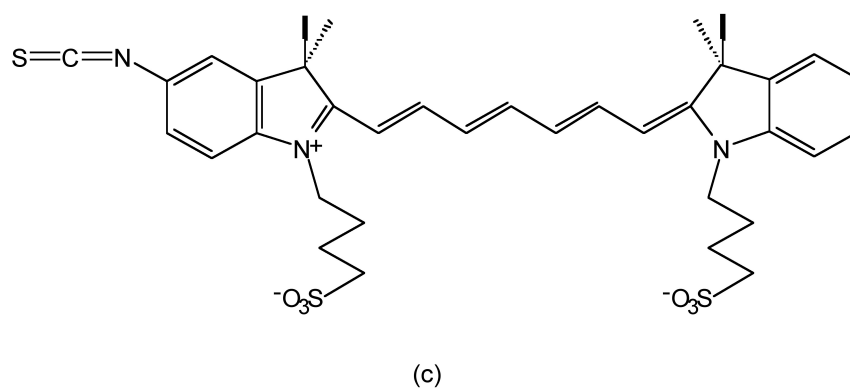
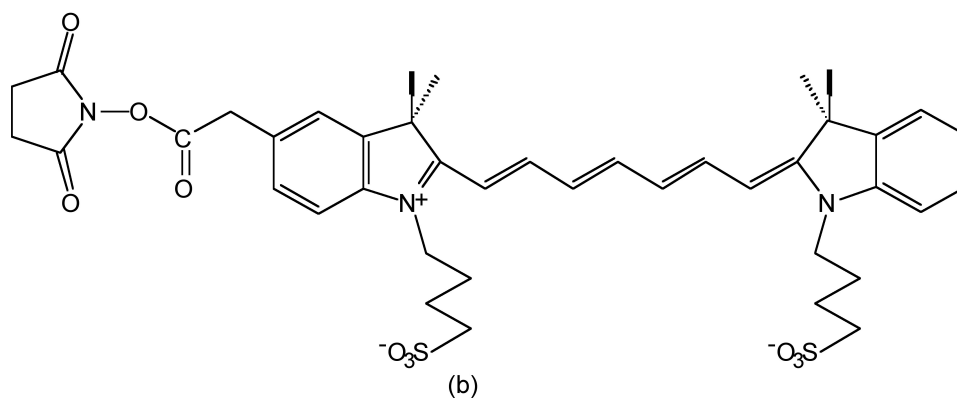
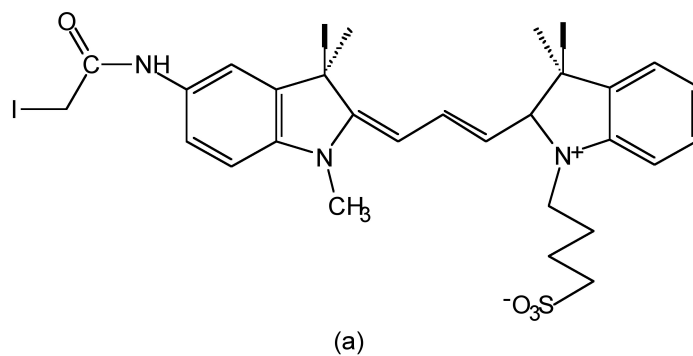


Figure 3.98: The structure of (a) Cy-3-iodo acetamide, (b) Cy-5-N-hydroxysuccinimide and (c) Cy-7-isothiocyanate.

3.5.2.3.4 Long-lifetime fluorophores

Almost all of the fluorophores mentioned above are organic fluorophores that have relative short lifetime from 1-10 ns. However, there are also a few long-lifetime organic fluorophore, such as pyrene and coronene with lifetime near 400 ns and 200 ns respectively (Figure 3.99). Long-lifetime is one of the important properties to fluorophores. With its help, the autofluorescence in biological system can be removed adequately, and hence improve the detectability over background.

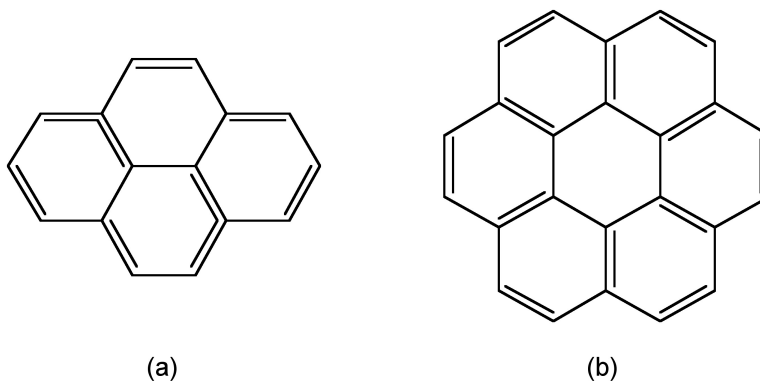


Figure 3.99: Structures of (a) pyrene and (b) coronene.

Although their emission belongs to phosphorescence, transition metal complexes are a significant class of long-lifetime fluorophores. Ruthenium (II), iridium (III), rhenium (I), and osmium (II) are the most popular transition metals that can combine with one to three diimine ligands to form fluorescent metal complexes. For example, iridium forms a cationic complex with two phenyl pyridine and one diimine ligand (Figure 3.100). This complex has excellent quantum yield and relatively long lifetime.

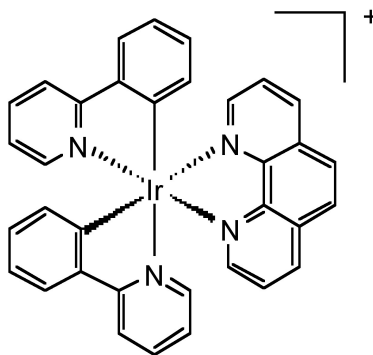


Figure 3.100: The structure of the cationic iridium complex, (ppy)₂Ir(phen).

3.5.2.4 Applications

With advances in fluorometers and fluorophores, fluorescence has been a dominant technology in the medical field, such clinic diagnosis and flow cytometry. Herein, the application of fluorescence in DNA and RNA detection is discussed.

The low concentration of DNA and RNA sequences in cells determine that high sensitivity of the probe is required, while the existence of various DNA and RNA with similar structures requires a high selectivity. Hence, fluorophores were introduced as the signal group into probes, because fluorescence spectroscopy is most sensitive technology until now.

The general design of a DNA or RNA probe involves using an antisense hybridization oligonucleotide to monitor target DNA sequence. When the oligonucleotide is connected with the target DNA, the signal groups-the fluorophores-emit designed fluorescence. Based on fluorescence spectroscopy, signal fluorescence can be detected which help us to locate the target DNA sequence. The selectively inherent in the hybridization between two complementary DNA/RNA sequences make this kind of DNA probes extremely high selectivity. A molecular Beacon is one kind of DNA probes. This simple but novel design is reported by Tyagi and Kramer in 1996 (Figure 3.101) and gradually developed to be one of the most common DNA/RNA probes.

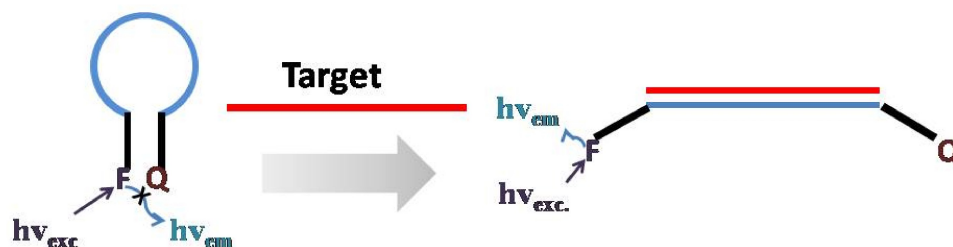


Figure 3.101: The structure of molecular beacon and its detecting mechanism.

Generally speaking, a molecular beacon it is composed of three parts: one oligonucleotide, a fluorophore and a quencher at different ends. In the absence of the target DNA, the molecular beacon is folded like a hairpin due to the interaction between the two series nucleotides at opposite ends of the oligonucleotide. At this time, the fluorescence is quenched by the close quencher. However, in the presence of the target, the probe region of the MB will hybridize to the target DNA, open the folded MB and separate the fluorophore and quencher. Therefore, the fluorescent signal can be detected which indicate the existence of a particular DNA.

3.5.2.5 Bibliography

- J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, 3rd ed, Springer (2006).
- A. A. Martí, S. Jockusch, N. Stevens, J. Ju, and N. J. Turro, *Acc. Chem. Res.*, 2007, **40**, 402.
- S. Tyagi and F. R. Kramer, *Nat. Biotechnol.*, 1996, **14**, 303.

3.6 Mossbauer Spectroscopy

3.6.1 Introduction to Mossbauer Spectroscopy¹⁴

3.6.1.1

In 1957 Rudolf Mossbauer achieved the first experimental observation of the resonant absorption and recoil-free emission of nuclear γ -rays in solids during his graduate work at the Institute for Physics of the Max Planck Institute for Medical Research in Heidelberg Germany. Mossbauer received the 1961 Nobel Prize in Physics for his research in resonant absorption of γ -radiation and the discovery of recoil-free emission a phenomenon that is named after him (http://nobelprize.org/nobel_prizes/physics/laureates/1961¹⁵ for more information about Rudolf Mossbauer and his nobel prize). The Mossbauer effect is the basis of Mossbauer spectroscopy.

The Mossbauer effect can be described very simply by looking at the energy involved in the absorption or emission of a γ -ray from a nucleus. When a free nucleus absorbs or emits a γ -ray to conserve momentum the nucleus must recoil, so in terms of energy:

$$E_{\gamma\text{-ray}} = E_{\text{nuclear transition}} - E_{\text{recoil}}$$

When in a solid matrix the recoil energy goes to zero because the effective mass of the nucleus is very large and momentum can be conserved with negligible movement of the nucleus. So, for nuclei in a solid matrix:

$$E_{\gamma\text{-ray}} = E_{\text{nuclear transition}}$$

This is the Mossbauer effect which results in the resonant absorption/emission of γ -rays and gives us a means to probe the hyperfine interactions of an atoms nucleus and its surroundings.

A Mossbauer spectrometer system consists of a γ -ray source that is oscillated toward and away from the sample by a “Mossbauer drive”, a collimator to filter the γ -rays, the sample, and a detector.

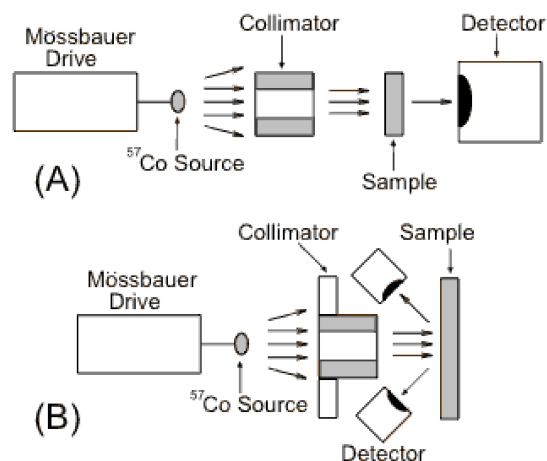


Figure 3.102: Schematic of Mossbauer Spectrometers. A = transmission; B = backscatter set up. Adapted from M. D. Dyar, D. G. Agresti, M. W. Schaefer, C. A. Grant, and E. C. Sklute, *Annu. Rev. Earth. Planet. Sci.*, 2006, **34**, 83. Copyright Annual Reviews (2006).

¹⁴This content is available online at <<http://cnx.org/content/m22328/1.7/>>.

¹⁵http://nobelprize.org/nobel_prizes/physics/laureates/1961

Figure 3.102 shows the two basic set ups for a Mossbauer spectrometer. The Mossbauer drive oscillates the source so that the incident γ -rays hitting the absorber have a range of energies due to the doppler effect. The energy scale for Mossbauer spectra (x-axis) is generally in terms of the velocity of the source in mm/s. The source shown (^{57}Co) is used to probe ^{57}Fe in iron containing samples because ^{57}Co decays to ^{57}Fe emitting a γ -ray of the right energy to be absorbed by ^{57}Fe . To analyze other Mossbauer isotopes other suitable sources are used. Fe is the most common element examined with Mossbauer spectroscopy because its ^{57}Fe isotope is abundant enough (2.2), has a low energy γ -ray, and a long lived excited nuclear state which are the requirements for observable Mossbauer spectrum. Other elements that have isotopes with the required parameters for Mossbauer probing are seen in Table 3.13.

Most commonly examined elements	Fe, Ru, W, Ir, Au, Sn, Sb, Te, I, W, Ir, Au, Eu, Gd, Dy, Er, Yb, Np
Elements that exhibit Mossbauer effect	K, Ni, Zn, Ge, Kr, Tc, Ag, Xe, Cs, Ba, La, Hf, Ta, Re, Os, Pt, Hg, Ce, Pr, Nd, Sm, Tb, Ho, Tm, Lu, Th, Pa, U, Pu, Am

Table 3.13: Elements with known Mossbauer isotopes and most commonly examined with Mossbauer spectroscopy.

3.6.1.1.1 Mossbauer spectra

The primary characteristics looked at in Mossbauer spectra are isomer shift (IS), quadrupole splitting (QS), and magnetic splitting (MS or hyperfine splitting). These characteristics are effects caused by interactions of the absorbing nucleus with its environment.

Isomer shift is due to slightly different nuclear energy levels in the source and absorber due to differences in the s-electron environment of the source and absorber. The oxidation state of an absorber nucleus is one characteristic that can be determined by the IS of a spectra. For example due to greater d electron screening Fe^{2+} has less s-electron density than Fe^{3+} at its nucleus which results in a greater positive IS for Fe^{2+} .

For absorbers with nuclear angular momentum quantum number $I > \frac{1}{2}$ the non-spherical charge distribution results in quadrupole splitting of the energy states. For example Fe with a transition from $I=1/2$ to $3/2$ will exhibit doublets of individual peaks in the Mossbauer spectra due to quadrupole splitting of the nuclear states as shown in red in Figure 3.103.

In the presence of a magnetic field the interaction between the nuclear spin moments with the magnetic field removes all the degeneracy of the energy levels resulting in the splitting of energy levels with nuclear spin I into $2I + 1$ sublevels. Using Fe for an example again, magnetic splitting will result in a sextet as shown in green in Figure 3.103. Notice that there are 8 possible transitions shown, but only 6 occur. Due to the selection rule $\Delta m_I = 0, 1$, the transitions represented as black arrows do not occur.

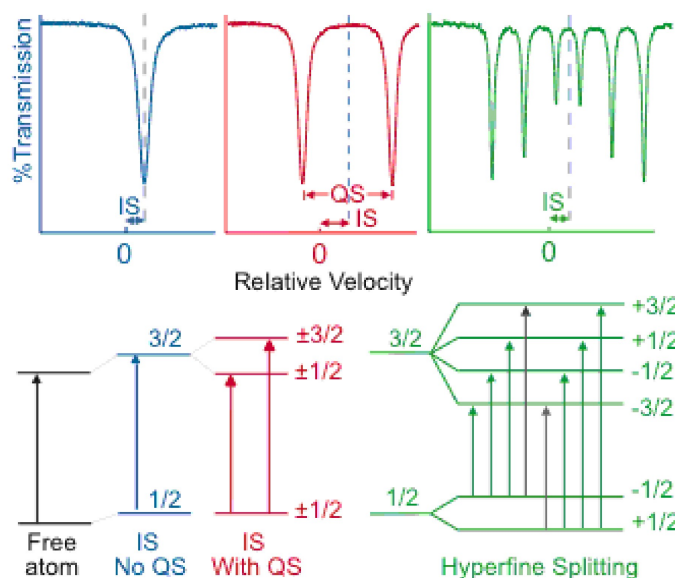


Figure 3.103: Characteristics of Mossbauer spectra related to nuclear energy levels. Adapted from M. D. Dyar, D. G. Agresti, M. W. Schaefer, C. A. Grant, and E. C. Sklute, *Annu. Rev. Earth. Planet. Sci.*, 2006, **34**, 83. Copyright Annual Reviews (2006).

3.6.1.2 Bibliography

- G. Wertheim. *Mossbauer Effect: Principles and Applications*. New York: Academic Press Inc. (1964).
- D. P. E. Dickson and F. J. Berry. *Mossbauer Spectroscopy*. New York: Cambridge University Press (1986).
- A. G. Maddock. *Mossbauer Spectroscopy: Principles and Applications of the Techniques*. England: Horwood Publishing Limited (1997).
- M. D. Dyar, D. G. Agresti, M. W. Schaefer, C. A. Grant, and E. C. Sklute, *Annu. Rev. Earth. Planet. Sci.*, 2006, **34**, 83.

3.6.2 Synthesis of Magnetite Nanoparticles¹⁶

Numerous schemes have been devised to synthesize magnetite nanoparticles (nMag). The different methods of nMag synthesis can be generally grouped as aqueous or non-aqueous according to the solvents used. Two of the most widely used and explored methods for nMag synthesis are the aqueous co-precipitation method and the non-aqueous thermal decomposition method.

The co-precipitation method of nMag synthesis consists of precipitation of Fe_3O_4 (nMag) by addition of a strong base to a solution of Fe^{2+} and Fe^{3+} salts in water. This method is very simple, inexpensive and produces highly crystalline nMag. The general size of nMag produced by co-precipitation is in the 15 to 50

¹⁶This content is available online at <<http://cnx.org/content/m22167/1.6/>>.

nm range and can be controlled by reaction conditions, however a large size distribution of nanoparticles is produced by this method. Aggregation of particles is also observed with aqueous methods.

The thermal decomposition method consists of the high temperature thermal decomposition of an iron-oleate complex derived from an iron precursor in the presence of surfactant in a high boiling point organic solvent under an inert atmosphere. For the many variations of this synthetic method many different solvents and surfactants are used. However, in most every method nMag is formed through the thermal decomposition of an iron-oleate complex to form highly crystalline nMag in the 5 to 40 nm range with a very small size distribution. The size of nMag produced is a function of reaction temperature, the iron to surfactant ratio, and the reaction time, and various methods are used that achieve good size control by manipulation of these parameters. The nMag synthesized by organic methods is soluble in organic solvents because the nMag is stabilized by a surfactant surface coating with the polar head group of the surfactant attached to and the hydrophobic tail extending away from the nMag (Figure 3.104). An example of a thermal decomposition method is shown in Figure 3.104.

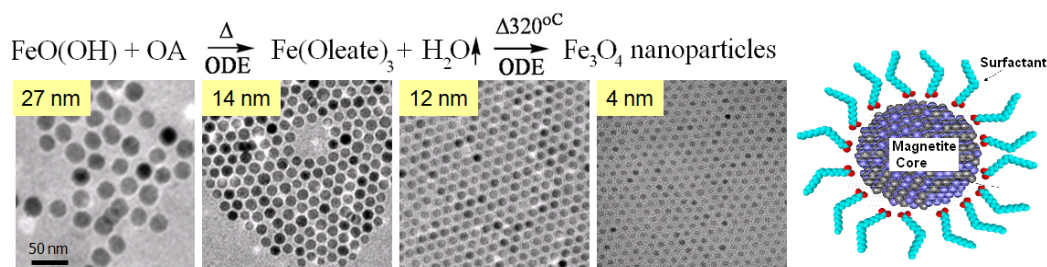


Figure 3.104: Top - The reaction equation for this method shows the iron precursor = iron oxo-hydrate, surfactant = oleic acid (OA), and solvent = 1-octadecene. The intermediate iron-oleate complex which thermally decomposes to nMag is formed upon heating the reaction mixture to the 320 °C reaction temperature. Bottom - TEM images showing size control by reaction time (time decreases left to right, constant molar ratio Fe:OA = 1:4 mol, and constant reaction temp T = 320 °C) and small size distribution of nMag. Right - Cartoon of surfactant coated nMag.

3.6.2.1 Bibliography

- A. Vioux, *Chem. Mater.* , 1997, **9** , 2292.

3.6.3 Mossbauer Analysis of Iron Oxide Nanoparticles¹⁷

3.6.3.1 Spectra and formula calculations

Due to the potential applications of magnetite nanoparticles (Fe_3O_4 , nMag) many methods have been devised for its synthesis. However, stoichiometric Fe_3O_4 is not always achieved by different synthetic methods. B-site vacancies introduced into the cubic inverse spinel crystal structure of nMag result in nonstoichiometric iron oxide of the formula $(\text{Fe}^{3+})_A(\text{Fe}_{(1-3x)}^{2+} \text{Fe}_{(1+2x)}^{3+} \text{O}_x)_B\text{O}_4$ where O represents B-site vacancy. The magnetic susceptibility which is key to most nMag applications decreases with increased B-site vacancy hence the extent of B-site vacancy is important. The very high sensitivity of the Mossbauer spectrum to the oxidation state and site occupancy of Fe^{3+} in cubic inverse spinel iron oxides makes Mossbauer spectroscopy valuable for addressing the issues of whether or not the product of a synthetic method is actually nMag and the extent of B-site vacancy.

¹⁷This content is available online at <<http://cnx.org/content/m22619/1.3/>>.

As with most analysis using multiple instrumental methods in conjunction is often helpful. This is exemplified by the use of XRD along with Mossbauer spectroscopy in the following analysis. Figure 3.105 shows the XRD results and Mossbauer spectra “magnetite” samples prepared by a $\text{Fe}^{2+}/\text{Fe}^{3+}$ co-precipitation (Mt025), hematite reduction by hydrogen (MtH2) and hematite reduction with coal (MtC). The XRD analysis shows MtH2 and MT025 exhibiting only magnetite peaks while MtC shows the presence of magnetite, maghemite, and hematite. This information becomes very useful when fitting peaks to the Mossbauer spectra because it gives a chemical basis for peak fitting parameters and helps to fit the peaks correctly.

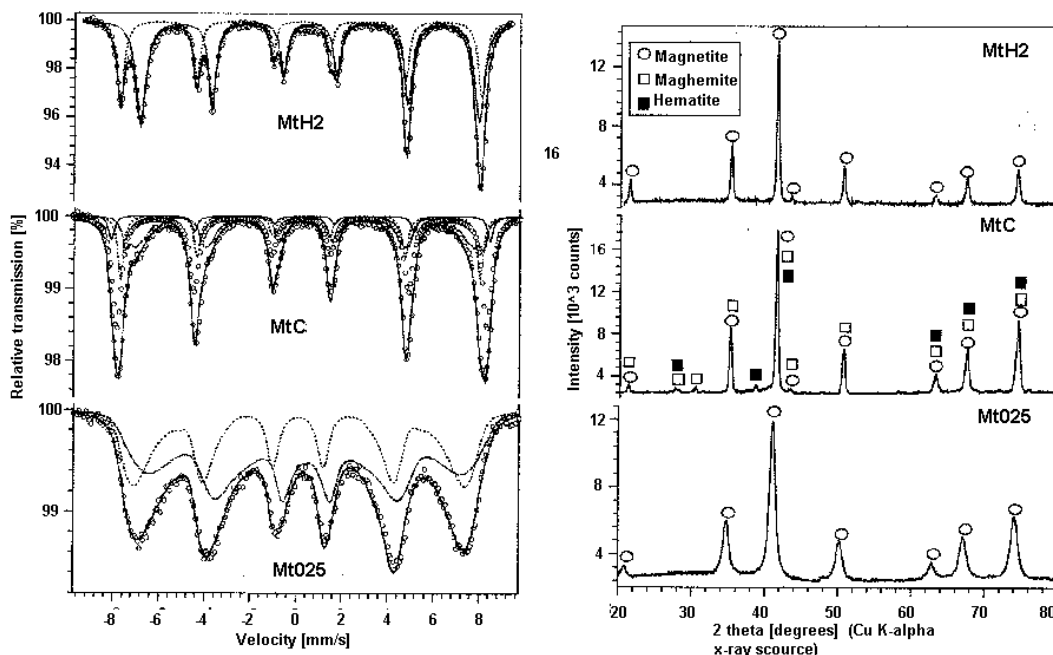


Figure 3.105: Mossbauer spectra (left) and corresponding XRD spectra of iron oxide sample prepared by different methods. Adapted from A. L. Andrade, D. M. Souza, M. C. Pereira, J. D. Fabris, and R. Z. Domingues. *J. Nanosci. Nanotechnol.*, 2009, **9**, 2081.

Being that the iron occupies two local environments, the A-site and B site, and two species (Fe^{2+} and Fe^{3+}) occupy the B-site one might expect the spectrum to be a combination of 3 spectra, however delocalization of electrons or electron hopping between Fe^{2+} and Fe^{3+} in the B site causes the nuclei to sense an average valence in the B site thus the spectrum are fitted with two curves accordingly. This is most easily seen in the Mt025 spectrum. The two fitted curves correspond to Fe^{3+} in the A-site and mixed valance $\text{Fe}^{2.5+}$ in the B-site. The isomer shift of the fitted curves can be used to determined which curve corresponds to which valence. The isomer shift relative to the top fitted curve is reported to be 0.661 and the bottom fitted curve is 0.274 relative to αFe thus the top fitted curve corresponds to less s-electron dense $\text{Fe}^{2.5+}$. The magnetic splitting is quite apparent. In each of the spectra, six peaks are present due to magnetic splitting of the nuclear energy states as explained previously. Quadrupole splitting is not so apparent, but actually is present in the spectra. The three peaks to the left of the center of a spectrum should be spaced the same as those to the right due to magnetic splitting alone since the energy level spacing between sublevels is equal. This is not the case in the above spectra, because the higher energy $I = 3/2$ sublevels are split unevenly due

to magnetic and quadrupole splitting interactions.

Once the peaks have been fitted appropriately, determination of the extent of B-site vacancy in $(\text{Fe}^{3+})_A(\text{Fe}_{(1-3x)}^{2+} \text{Fe}_{(1+2x)}^{3+}\text{O}_x)_B\text{O}_4$ is a relatively simple matter. All one has to do to determine the number of vacancies (x) is solve the equation:

$\frac{RA_B}{RA_A} = \frac{2-6x}{1-5x}$ where RA_B or RA_A = relative area ($\frac{\text{Area A or B site curve}}{\text{Area of both curves}}$) of the curve for the B or A site respectively

The reasoning for this equation is as follows. Taking into account that the mixed valance $\text{Fe}^{2.5+}$ curve is a result of paired interaction between Fe^{2+} and Fe^{3+} the nonstoichiometric chemical formula is $(\text{Fe}^{3+})_A(\text{Fe}_{(1-3x)}^{2+} \text{Fe}_{(1+2x)}^{3+}\text{O}_x)_B\text{O}_4$. The relative intensity (or relative area) of the Fe-A and Fe-B curves is very sensitive to stoichiometry because vacancies in the B-site reduce the Fe-A curve and increase Fe-B curve intensities. This is due to the unpaired Fe_{5x}^{3+} adding to the intensity of the Fe-A curve rather than the Fe-B curve. Since the relative area is directly proportional to the number of Fe contributing to the spectrum the ratio of the relative areas is equal to stoichiometric ratio of $\text{Fe}^{2.5+}$ to Fe^{3+} , which yields the above formula.

Example Calculation:

For MtH2 $RA_A/RA_B = 1.89$

Plugging x into the nonstoichiometric iron oxide formula yeilds:

$$\frac{RA_B}{RA_A} = \frac{2-6x}{1-5x} \quad \text{solving for x yeilds} \quad x = \frac{2 - \frac{RA_A}{RA_B}}{5 \frac{RA_A}{RA_B} + 6} = \frac{2-1.89}{5(1.89)+6} = 0.00712$$

$(\text{Fe}^{3+})_A(\text{Fe}_{1.9572}^{2+} \text{Fe}_{0.0356}^{3+})_B\text{O}_4$ (very close to stoichiometric)

Sample	RA_B/RA_A	X	Chemical formula
MtH2	1.89	0.007	$(\text{Fe}^{3+})_A(\text{Fe}_{0.979}^{2+} \text{Fe}_{1.014}^{3+})_B\text{O}_4$
MtC	1.66	0.024	$(\text{Fe}^{3+})_A(\text{Fe}_{0.929}^{2+} \text{Fe}_{1.048}^{3+})_B\text{O}_4$
Mt025	1.60	0.029	$(\text{Fe}^{3+})_A(\text{Fe}_{0.914}^{2+} \text{Fe}_{1.057}^{3+})_B\text{O}_4$

Table 3.14: Parameters and nonstoichiometric formulas for MtC, Mt025, and MtH2

3.6.3.2 Bibliography

- F. C. Voogt, T. Fujii, P. J. M. Smulders, L. Niesen, M. A. James, and T. Hibma, *Phys. Rev. B*, 1999, **60**, 11193.
- A. L. Andrade, D. M. Souza, M. C. Pereira, J. D. Fabris, and R. Z. Domingues, *J. Nanosci. Nanotechnol.*, 2009, **9**, 2081.
- J. B. Yang, X. D. Zhou, W. B. Yelon, W. fJ. James, Q. Cai, K. V. Gopalakrishnan, S. K. Malik, X. C. Sun, and D. E. Nikles, *J. Appl. Phys.*, 2004, **95**, 7540.
- R.E. Vandenberghe, I. Nedkov, T. Merodiiska, and L. Slavov, *Hyperfine Interact.* 2005, **165**, 267.

3.6.4 Determining the Chemical Formula of Nonstoichiometric Iron Oxide Nanoparticles by Mossbauer Spectroscopy¹⁸

3.6.4.1 Chemical formula determination

Magnetite (Fe_3O_4) nanoparticles (n-Mag) are nanometer sized, superparamagnetic, have high saturation magnetization, high magnetic susceptibility, and low toxicity. These properties could be utilized for many

¹⁸This content is available online at <<http://cnx.org/content/m22184/1.4/>>.

possible applications; hence, n-Mag has attracted much attention in the scientific community. Some of the potential applications include drug delivery, hyperthermia agents, MRI contrast agents, cell labeling, and cell separation to name a few.

The crystal structure of n-Mag is cubic inverse spinel with Fe^{3+} cations occupying the interstitial tetrahedral sites(A) and Fe^{3+} along with Fe^{2+} occupying the interstitial octahedral sites(B) of an FCC lattice of O^{2-} . Including the site occupation and charge of Fe, the n-Mag chemical formula can be written $(\text{Fe}^{3+})_A(\text{Fe}^{2+}\text{Fe}^{3+})_B\text{O}_4$. Non-stoichiometric iron oxide results from B-site vacancies in the crystal structure. To maintain balanced charge and take into account the degree of B-site vacancies the iron oxide formula is written $(\text{Fe}^{3+})_A(\text{Fe}_{(1-3x)})^{2+}\text{Fe}_{(1+2x)}^{3+}\text{O}_x)_B\text{O}_4$ where O represents B-site vacancy. The extent of B-site vacancy has a significant effect on the magnetic properties of iron oxide and in the synthesis of n-Mag stoichiometric iron oxide is not guaranteed; therefore, B-site vacancy warrants attention in iron oxide characterization, and can be addressed using Mossbauer spectroscopy.

3.7 NMR Spectroscopy

3.7.1 Introduction to Nuclear Magnetic Resonance Spectroscopy¹⁹

3.7.1.1 Introduction

Nuclear magnetic resonance spectroscopy (NMR) is a widely used and powerful method that takes advantage of the magnetic properties of certain nuclei. The basic principle behind NMR is that some nuclei exist in specific nuclear spin states when exposed to an external magnetic field. NMR observes transitions between these spin states that are specific to the particular nuclei in question, as well as that nuclei's chemical environment. However, this only applies to nuclei whose spin, I , is not equal to 0, so nuclei where $I = 0$ are 'invisible' to NMR spectroscopy. These properties have led to NMR being used to identify molecular structures, monitor reactions, study metabolism in cells, and is used in medicine, biochemistry, physics, industry, and almost every imaginable branch of science.

3.7.1.2 Theory

The chemical theory that underlies NMR spectroscopy depends on the intrinsic spin of the nucleus involved, described by the quantum number S . Nuclei with a non-zero spin are always associated with a non-zero magnetic moment, as described by (3.8), where μ is the magnetic moment, S is the spin, and γ is always non-zero. It is this magnetic moment that allows for NMR to be used; therefore nuclei whose quantum spin is zero cannot be measured using NMR. Almost all isotopes that have both an even number of protons and neutrons have no magnetic moment, and cannot be measured using NMR.

$$\mu = \gamma.S \quad (3.8)$$

In the presence of an external magnetic field (B) for a nuclei with a spin $I = 1/2$, there are two spin states present of $+1/2$ and $-1/2$. The difference in energy between these two states at a specific external magnetic field (B_x) are given by (3.9), and are shown in Figure 3.106, where E is energy, I is the spin of the nuclei, and μ is the magnetic moment of the specific nuclei being analyzed. The difference in energy shown is always extremely small, so for NMR strong magnetic fields are required to further separate the two energy states. At the applied magnetic fields used for NMR, most magnetic resonance frequencies tend to fall in the radio frequency range.

$$E = \mu.B_x/I \quad (3.9)$$

¹⁹This content is available online at <<http://cnx.org/content/m38356/1.1/>>.

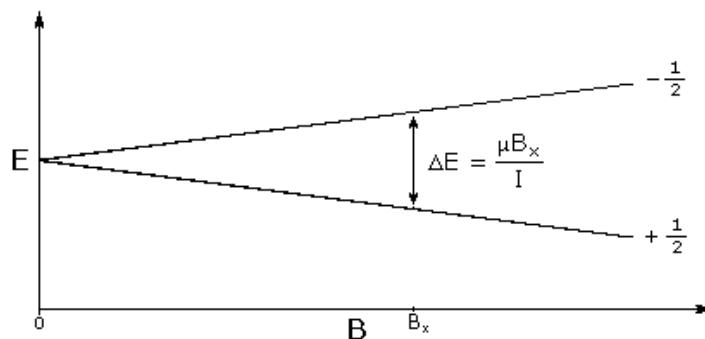


Figure 3.106: The difference in energy between two spin states over a varying magnetic field B.

The reason NMR can differentiate between different elements and isotopes is due to the fact that each specific nuclide will only absorb at a very specific frequency. This specificity means that NMR can generally detect one isotope at a time, and this results in different types of NMR: such as ^1H NMR, ^{13}C NMR, and ^{31}P NMR, to name only a few.

The subsequent absorbed frequency of any type of nuclei is not always constant, since electrons surrounding a nucleus can result in an effect called nuclear shielding, where the magnetic field at the nucleus is changed (usually lowered) because of the surrounding electron environment. This differentiation of a particular nucleus based upon its electronic (chemical) environment allows NMR be used to identify structure. Since nuclei of the same type in different electron environments will be more or less shielded than another, the difference in their environment (as observed by a difference in the surrounding magnetic field) is defined as the chemical shift.

3.7.1.3 Instrumentation

An example of an NMR spectrometer is given in Figure 3.107. NMR spectroscopy works by varying the machine's emitted frequency over a small range while the sample is inside a constant magnetic field. Most of the magnets used in NMR machines to create the magnetic field range from 6 to 24 T. The sample is placed within the magnet and surrounded by superconducting coils, and is then subjected to a frequency from the radio wave source. A detector then interprets the results and sends it to the main console.

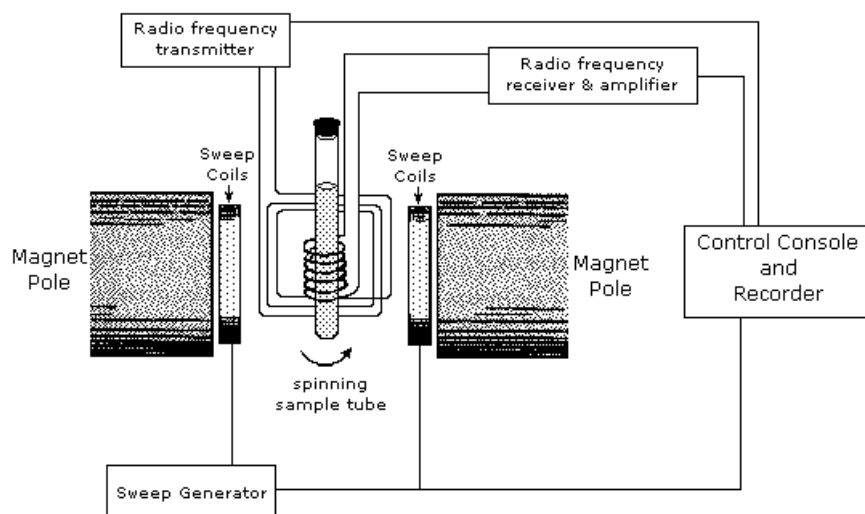


Figure 3.107: Diagram of an NMR spectrometer.

3.7.1.4 Interpreting NMR spectra

3.7.1.4.1 Chemical shift

The different local chemical environments surrounding any particular nuclei causes them to resonate at slightly different frequencies. This is a result of a nucleus being more or less shielded than another. This is called the chemical shift (δ). One factor that affects chemical shift is the changing of electron density from around a nucleus, such as a bond to an electronegative group. Hydrogen bonding also changes the electron density in ^1H NMR, causing a larger shift. These frequency shifts are miniscule in comparison to the fundamental NMR frequency differences, on a scale of Hz as compared to MHz. For this reason chemical shifts (δ) are described by the unit ppm on an NMR spectra, (3.10), where H_{ref} = the resonance frequency of the reference, H_{sub} = resonance frequency of the substance, and H_{machine} = operating frequency of the spectrometer.

$$\delta = \left(\frac{H_{\text{ref}} - H_{\text{sub}}}{H_{\text{machine}}} \right) \times 10^6 \quad (3.10)$$

Since the chemical shift (δ in ppm) is reported as a relative difference from some reference frequency, so a reference is required. In ^1H and ^{13}C NMR, for example, tetramethylsilane (TMS, $\text{Si}(\text{CH}_3)_4$) is used as the reference. Chemical shifts can be used to identify structural properties in a molecule based on our understanding of different chemical environments. Some examples of where different chemical environments fall on a ^1H NMR spectra are given in Table 3.15.

Functional group	Chemical shift range (ppm)
Alkyl (e.g., methyl -CH ₃)	~ 1
Alkyl adjacent to oxygen (-CH ₂ -O)	3 - 4
Alkene (=CH ₂)	~ 6
Alkyne (C-H)	~ 3
Aromatic	7 - 8

Table 3.15: Representative chemical shifts for organic groups in the ¹H NMR.

In Figure 3.108, an ¹H NMR spectra of ethanol, we can see a clear example of chemical shift. There are three sets of peaks that represent the six hydrogens of ethanol (C₂H₆O). The presence of three sets of peaks means that there are three different chemical environments that the hydrogens can be found in: the terminal methyl (CH₃) carbon's three hydrogens, the two hydrogens on the methylene (CH₂) carbon adjacent to the oxygen, and the single hydrogen on the oxygen of the alcohol group (OH). Once we cover spin-spin coupling, we will have the tools available to match these groups of hydrogens to their respective peaks.

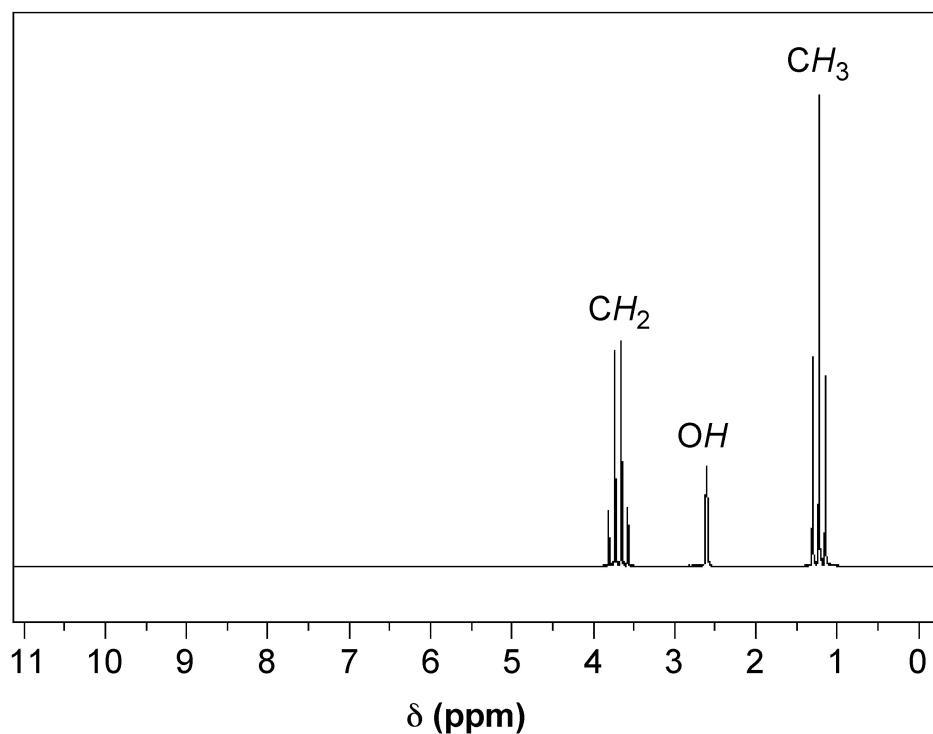


Figure 3.108: A ¹H NMR spectra of ethanol (CH₃CH₂OH).

3.7.1.5 Limitations of NMR

Despite all of its upsides, there are several limitations that can make NMR analysis difficult or impossible in certain situations. One such issue is that the desired isotope of an element that is needed for NMR analysis may have little or no natural abundance. For example the natural abundance of ^{13}C , the active isotope for carbon NMR, is about 11%, which works well for analysis. However, in the case of oxygen the active isotope for NMR is ^{17}O , which is only 0.035% naturally abundant. This means that there are certain elements that can essentially never be measured through NMR.

Another problem is that some elements have an extremely low magnetic moment, μ . The sensitivity of NMR machines is based on the magnetic moment of the specific element, but if the magnetic moment is too low it can be very difficult to obtain an NMR spectra with enough peak intensity to properly analyze.

3.7.1.6 Bibliography

- D. L. Nelson and M. M. Cox, *Principles of Biochemistry*, 5th Ed, W. H. Freeman and Company, New York (2008).
- D. F. Shriver and P. W. Atkins, *Inorganic Chemistry*, 4th Ed, Oxford University Press (2006).
- I. C. P. Smith and D. E. Blandford, *Anal. Chem.*, 1995, **67**, 509.

3.7.2 NMR Properties of the Elements²⁰

Isotope	Natural abundance (%)	Relative NMR frequency (MHz)	Relative receptivity as compared to ^1H
^1H	99.985	100	1.00
^3H	-	106.7	-
^3He	0.00013	76.2	5.8×10^{-7}
^{13}C	1.11	25.1	1.8×10^{-4}
^{15}N	0.37	10.1	3.9×10^{-6}
^{19}F	100	94.1	8.3×10^{-1}
^{29}Si	4.7	19.9	3.7×10^{-4}
^{31}P	100	40.5	6.6×10^{-2}
^{57}Fe	2.2	3.2	7.4×10^{-7}
^{77}Se	7.6	19.1	5.3×10^{-4}
^{89}Y	100	4.9	1.2×10^{-4}
^{103}Rh	100	3.2	3.2×10^{-5}
^{107}Ag	51.8	4.0	3.5×10^{-5}

continued on next page

²⁰This content is available online at <<http://cnx.org/content/m34632/1.1/>>.

^{109}Ag	48.2	4.7	4.9×10^{-5}
^{111}Cd	12.8	21.2	1.2×10^{-3}
^{113}Cd	12.3	22.2	1.3×10^{-3}
$^{117}\text{Sn}^{\text{a}}$	7.6	35.6	3.5×10^{-3}
^{119}Sn	8.6	37.3	4.5×10^{-3}
$^{125}\text{Te}^{\text{a}}$	7.0	31.5	2.2×10^{-3}
^{129}Xe	26.4	27.8	5.7×10^{-3}
^{169}Tm	100	8.3	5.7×10^{-4}
^{171}Yb	14.3	17.6	7.8×10^{-4}
^{183}W	14.4	4.2	1.1×10^{-5}
^{187}Os	1.6	2.3	2.0×10^{-7}
^{195}Pt	33.8	21.4	3.4×10^{-3}
^{199}Hg	16.8	17.9	9.8×10^{-4}
^{203}Tl	29.5	57.1	5.7×10^{-2}
^{205}Tl	70.5	57.6	1.4×10^{-1}
^{207}Pb	22.6	20.9	2.0×10^{-1}

Table 3.16: NMR properties of selected spin $1/2$ nuclei. ^a Other spin $1/2$ also exist.

Isotope	Spin	Natural abundance (%)	Relative NMR frequency (MHz)	Relative receptivity as compared to ^1H	Quadrupole moment (10^{-28} m^2)
^2H	1	0.015	15.4	1.5×10^{-6}	2.8×10^{-3}
^6Li	1	7.4	14.7	6.3×10^{-4}	-8×10^{-4}
^7Li	$3/2$	92.6	38.9	2.7×10^{-1}	-4×10^{-2}
^9Be	$3/2$	100	14.1	1.4×10^{-2}	5×10^{-2}
^{10}B	3	19.6	10.7	3.9×10^{-3}	8.5×10^{-2}
^{11}B	$3/2$	80.4	32.1	1.3×10^{-1}	4.1×10^{-2}
^{14}Na	1	99.6	7.2	1.0×10^{-3}	1×10^{-2}
^{17}O	$5/2$	0.037	13.6	1.1×10^{-5}	-2.6×10^{-2}
^{23}Na	$5/2$	100	26.5	9.3×10^{-2}	1×10^{-1}
<i>continued on next page</i>					

²⁵ Mg	⁵ / ₂	10.1	6.1	2.7 x 10 ⁻⁴	2.2 x 10 ⁻¹
²⁷ Al	⁵ / ₂	100	26.1	2.1 x 10 ⁻¹	1.5 x 10 ⁻¹
³³ S	³ / ₂	0.76	7.7	1.7 x 10 ⁻⁵	-5.5 x 10 ⁻²
³⁵ Cl	³ / ₂	75.5	9.8	3.6 x 10 ⁻³	-1 x 10 ⁻¹
³⁷ Cl	³ / ₂	24.5	8.2	6.7 x 10 ⁻⁴	-7.9 x 10 ⁻²
³⁹ K ^b	³ / ₂	93.1	4.7	4.8 x 10 ⁻⁴	4.9 x 10 ⁻²
⁴³ Ca	⁷ / ₂	0.15	6.7	8.7 x 10 ⁻⁶	2 x 10 ⁻¹
⁴⁵ Sc	⁷ / ₂	100	24.3	3.0 x 10 ⁻¹	-2.2 x 10 ⁻¹
⁴⁷ Ti	⁵ / ₂	7.3	5.6	1.5 x 10 ⁻⁴	2.9 x 10 ⁻¹
⁴⁹ Ti	⁷ / ₂	5.5	5.6	2.1 x 10 ⁻⁴	2.4 x 10 ⁻¹
⁵¹ V ^b	⁷ / ₂	99.8	26.3	3.8 x 10 ⁻¹	-5 x 10 ⁻²
⁵³ Cr	³ / ₂	9.6	5.7	8.6 x 10 ⁻⁵	3 x 10 ⁻²
⁵⁵ Mn	⁵ / ₂	100	24.7	1.8 x 10 ⁻¹	4 x 10 ⁻¹
⁵⁹ Co	⁷ / ₂	100	23.6	2.8 x 10 ⁻¹	3.8 x 10 ⁻¹
⁶¹ Ni	³ / ₂	1.2	8.9	4.1 x 10 ⁻¹	1.6 x 10 ⁻¹
⁶³ Cu	³ / ₂	69.1	26.5	6.5 x 10 ⁻²	-2.1 x 10 ⁻¹
⁶⁵ Cu	³ / ₂	30.9	28.4	3.6 x 10 ⁻²	-2.0 x 10 ⁻¹
⁶⁷ Zn	⁵ / ₂	4.1	6.3	1.2 x 10 ⁻⁴	1.6 x 10 ⁻¹
⁶⁹ Ga	³ / ₂	60.4	24.0	4.2 x 10 ⁻²	1.9 x 10 ⁻¹
⁷¹ Ga	³ / ₂	39.6	30.6	5.7 x 10 ⁻²	1.2 x 10 ⁻¹
⁷³ Ge	⁹ / ₂	7.8	3.5	1.1 x 10 ⁻⁴	-1.8 x 10 ⁻¹
⁷⁵ As	³ / ₂	100	17.2	2.5 x 10 ⁻²	2.9 x 10 ⁻¹
⁷⁹ Br	³ / ₂	50.5	25.1	4.0 x 10 ⁻²	3.7 x 10 ⁻¹
⁸¹ Br	³ / ₂	49.5	27.1	4.9 x 10 ⁻²	3.1 x 10 ⁻¹
⁸⁷ Rb ^b	³ / ₂	27.9	32.8	4.9 x 10 ⁻²	1.3 x 10 ⁻¹
⁸⁷ Sr	⁹ / ₂	7.0	4.3	1.9 x 10 ⁻⁴	3 x 10 ⁻¹
⁹¹ Zr	⁵ / ₂	11.2	9.3	1.1 x 10 ⁻³	-2.1 x 10 ⁻¹
⁹³ Nb	⁹ / ₂	100	24.5	4.9 x 10 ⁻¹	-2.2 x 10 ⁻¹
<i>continued on next page</i>					

⁹⁵ Mo	$5/2$	15.7	6.5	5.1×10^{-4}	$\pm 1.2 \times 10^{-1}$
⁹⁷ Mo	$5/2$	9.5	6.7	3.3×10^{-4}	± 1.1
⁹⁹ Ru	$5/2$	12.7	4.6	1.5×10^{-4}	7.6×10^{-2}
¹⁰¹ Ru	$5/2$	17.1	5.2	2.8×10^{-4}	4.4×10^{-1}
¹⁰⁵ Pd	$5/2$	22.2	4.6	2.5×10^{-4}	8×10^{-1}
¹¹⁵ In ^b	$9/2$	95.7	22.0	3.4×10^{-1}	8.3×10^{-1}
¹²¹ Sb	$5/2$	57.3	24.0	9.3×10^{-2}	-2.8×10^{-1}
¹²³ Sb	$7/2$	42.7	13.0	2.0×10^{-2}	-3.6×10^{-1}
¹²⁷ I	$5/2$	100	20.1	9.5×10^{-2}	-7.9×10^{-1}
¹³¹ Xe ^a	$3/2$	21.3	8.2	5.9×10^{-4}	-1.2×10^{-1}
¹³³ Cs	$7/2$	100	13.2	4.8×10^{-2}	-3×10^{-3}
¹³⁷ Ba ^b	$3/2$	11.3	11.1	7.9×10^{-4}	2.8×10^{-1}
¹³⁹ La	$7/2$	99.9	14.2	6.0×10^{-2}	2.2×10^{-1}
¹⁷⁷ Hf	$7/2$	18.5	4.0	2.6×10^{-4}	4.5
¹⁷⁹ Hf	$9/2$	13.8	2.5	7.4×10^{-5}	5.1
¹⁸¹ Ta	$7/2$	99.99	12.0	3.7×10^{-2}	3
¹⁸⁵ Re	$5/2$	37.1	22.7	5.1×10^{-2}	2.3
¹⁸⁷ Re	$5/2$	62.9	22.9	8.8×10^{-2}	2.2
¹⁸⁹ Os ^a	$3/2$	16.1	7.8	3.9×10^{-4}	8×10^{-1}
¹⁹¹ Ir	$3/2$	37.3	1.7	9.8×10^{-6}	1.1
¹⁹³ Ir	$3/2$	62.7	1.9	2.1×10^{-5}	1.0
¹⁹⁷ Au	$3/2$	100	1.7	2.6×10^{-5}	5.9×10^{-1}
²⁰¹ Hg	$3/2$	13.2	6.6	1.9×10^{-4}	4.4×10^{-1}
²⁰⁹ Bi	$9/2$	100	16.2	1.4×10^{-1}	-3.8×10^{-1}

Table 3.17: NMR properties of selected quadrupolar nuclei. ^a A spin $1/2$ isotope also exists. ^b Other quadrupolar nuclei exist.

3.7.3 NMR Spin Coupling²¹

3.7.3.1 The basis of spin coupling

Nuclear magnetic resonance (NMR) signals arise when nuclei absorb a certain radio frequency and are excited from one spin state to another. The exact frequency of electromagnetic radiation that the nucleus absorbs depends on the magnetic environment around the nucleus. This magnetic environment is controlled mostly by the applied field, but is also affected by the magnetic moments of nearby nuclei. Nuclei can be in one of many spin states (Figure 3.110), giving rise to several possible magnetic environments for the observed nucleus to resonate in. This causes the NMR signal for a nucleus to show up as a multiplet rather than a single peak.

²¹This content is available online at <<http://cnx.org/content/m43551/1.1/>>.

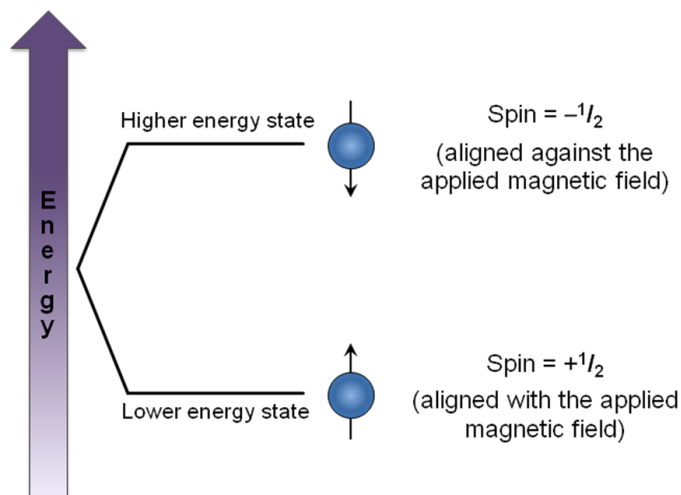


Figure 3.110: The different spin states of a nucleus ($I = 1/2$) in a magnetic field. These different states increase or decrease the effective magnetic field experienced by a nearby nucleus, allowing for two distinct signals.

When nuclei have a spin of $I = 1/2$ (as with protons), they can have two possible magnetic moments and thus split a single expected NMR signal into two signals. When more than one nucleus affects the magnetic environment of the nucleus being examined, complex multiplets form as each nucleus splits the signal into two additional peaks. If those nuclei are magnetically equivalent to each other, then some of the signals overlap to form peaks with different relative intensities. The multiplet pattern can be predicted by Pascal's triangle (Figure 3.111), looking at the n^{th} row, where n = number of nuclei equivalent to each other but *not* equivalent to the one being examined. In this case, the number of peaks in the multiplet is equal to $n + 1$

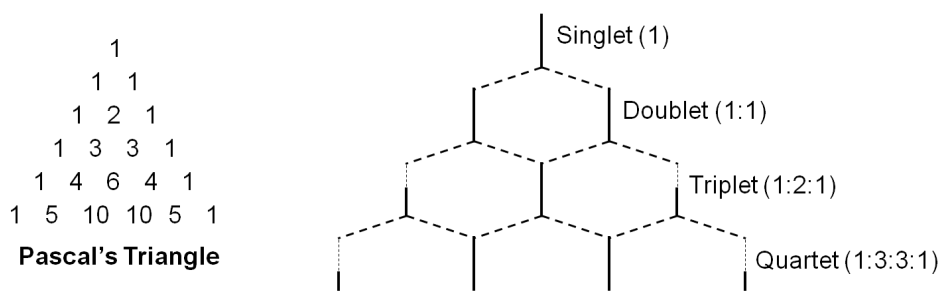


Figure 3.111: Pascal's triangle predicts the number of peaks in a multiplet and their relative intensities.

When there is more than one type of nucleus splitting an NMR signal, then the signal changes from a multiplet to a group of multiplets (Figure 3.112). This is caused by the different *coupling constants* associated with different types of nuclei. Each nucleus splits the NMR signal by a different width, so the

peaks no longer overlap to form peaks with different relative intensities.

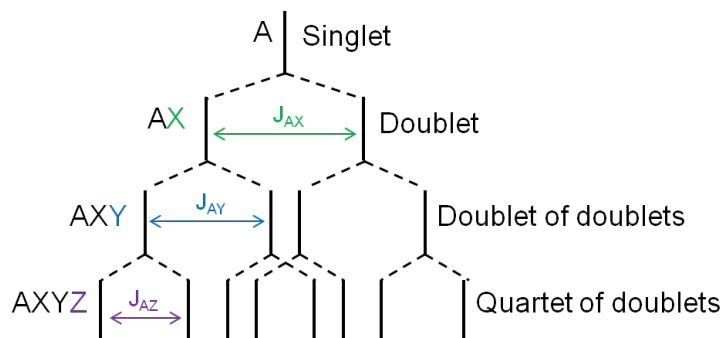


Figure 3.112: The splitting tree of different types of multiplets.

When nuclei have $I > \frac{1}{2}$, they have more than two possible magnetic moments and thus split NMR signals into more than two peaks. The number of peaks expected is $2I + 1$, corresponding to the number of possible orientations of the magnetic moment. In reality however, some of these peaks may be obscured due to quadrupolar relaxation. As a result, most NMR focuses on $I = \frac{1}{2}$ nuclei such as ^1H , ^{13}C , and ^{31}P .

Multiplets are centered around the chemical shift expected for a nucleus had its signal not been split. The total area of a multiplet corresponds to the number of nuclei resonating at the given frequency.

3.7.3.2 Spin coupling in molecules

Looking at actual molecules raises questions about which nuclei can cause splitting to occur. First of all, it is important to realize that only nuclei with $I \neq 0$ will show up in an NMR spectrum. When $I = 0$, there is only one possible spin state and obviously the nucleus cannot flip between states. Since the NMR signal is based on the absorption of radio frequency as a nucleus transitions from one spin state to another, $I = 0$ nuclei do not show up on NMR. In addition, they do not cause splitting of other NMR signals because they only have one possible magnetic moment. This simplifies NMR spectra, in particular of organic and organometallic compounds, greatly, since the majority of carbon atoms are ^{12}C , which have $I = 0$.

For a nucleus to cause splitting, it must be close enough to the nucleus being observed to affect its magnetic environment. The splitting technically occurs through bonds, not through space, so as a general rule, only nuclei separated by three or fewer bonds can split each other. However, even if a nucleus is close enough to another, it may not cause splitting. For splitting to occur, the nuclei must also be non-equivalent. To see how these factors affect real NMR spectra, consider the spectrum for chloroethane (Figure 3.113)

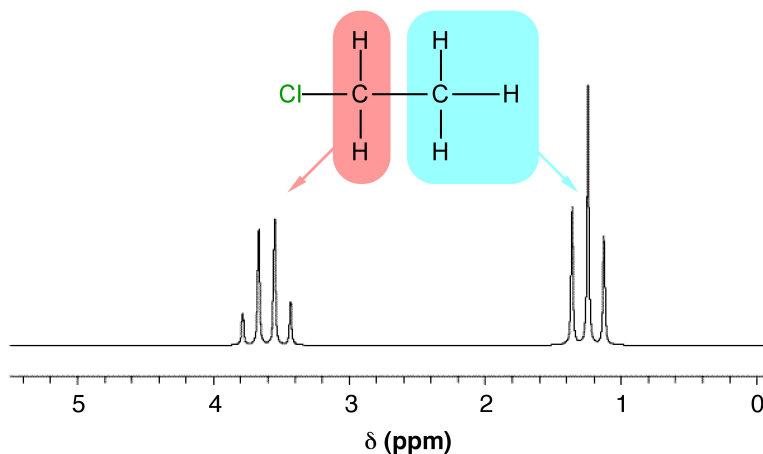


Figure 3.113: The NMR spectrum for chloroethane. Adapted from A. M. Castillo, L. Patiny, and J. Wist. *J. Magn. Reson.*, 2010, **209**, 123.

Notice that in Figure 3.113 there are two groups of peaks in the spectrum for chloroethane, a triplet and a quartet. These arise from the two different types of $I \neq 0$ nuclei in the molecule, the protons on the methyl and methylene groups. The multiplet corresponding to the CH_3 protons has a relative integration (peak area) of three (one for each proton) and is split by the two methylene protons ($n = 2$), which results in $n + 1$ peaks, i.e., 3 which is a triplet. The multiplet corresponding to the CH_2 protons has an integration of two (one for each proton) and is split by the three methyl protons ($n = 3$) which results in $n + 1$ peaks, i.e., 4 which is a quartet. Each group of nuclei splits the other, so in this way, they are *coupled*.

3.7.3.3 Coupling constants

The difference (in Hz) between the peaks of a multiplet is called the *coupling constant*. It is particular to the types of nuclei that give rise to the multiplet, and is independent of the field strength of the NMR instrument used. For this reason, the coupling constant is given in Hz, not ppm. The coupling constant for many common pairs of nuclei are known (Table 3.18), and this can help when interpreting spectra.

Structural type	Coupling constant (Hz)
	6 - 8
	5 - 7
	2 - 12
	0.5 - 3
	12 - 15
	12 - 18
	7 - 12
	0.5 - 3
	3 - 11
	2 - 3
	<i>ortho</i> = 6 - 9; <i>meta</i> = 1 - 3; <i>para</i> = 0 - 1

Table 3.18: Typical coupling constants for various organic structural types.

Coupling constants are sometimes written ^nJ to denote the number of bonds (n) between the coupled nuclei. Alternatively, they are written as $J(\text{H-H})$ or J_{HH} to indicate the coupling is between two hydrogen atoms. Thus, a coupling constant between a phosphorous atom and a hydrogen would be written as $J(\text{P-H})$ or J_{PH} . Coupling constants are calculated empirically by measuring the distance between the peaks of a multiplet, and are expressed in Hz.

Example 3.1

Coupling constants may be calculated from spectra using frequency or chemical shift data. Consider the spectrum of chloroethane shown in Figure 3.114 and the frequency of the peaks (collected on a 60 MHz spectrometer) given in Table 3.19.

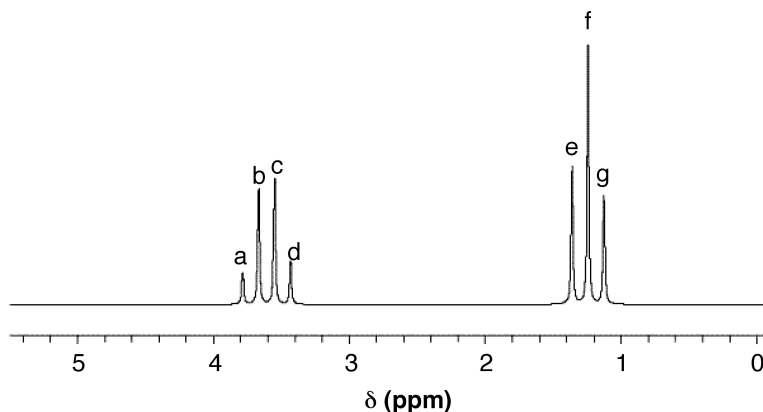


Figure 3.114: ^1H NMR spectrum of chloroethane. Peak positions for labeled peaks are given in Table 3.19.

Peak label	δ (ppm)	ν (Hz)
a	3.7805	226.83
b	3.6628	219.77
c	3.5452	212.71
d	3.4275	205.65
e	1.3646	81.88
f	1.2470	74.82
g	1.1293	67.76

Table 3.19: Chemical shift in ppm and Hz for all peaks in the ^1H NMR spectrum of chloroethane. Peak labels are given in Figure 3.114.

To determine the coupling constant for a multiplet (in this case, the quartet in Figure 3.114), the difference in frequency (ν) between each peak is calculated and the average of this value provides the coupling constant in Hz. For example using the data from Table 3.19:

Frequency of peak c - frequency of peak d = 212.71 Hz - 205.65 Hz = 7.06 Hz

Frequency of peak b - frequency of peak c = 219.77 Hz - 212.71 Hz = 7.06 Hz

Frequency of peak a - frequency of peak b = 226.83 Hz - 219.77 Hz = 7.06 Hz

Average: 7.06 Hz

$\therefore J(\text{H-H}) = 7.06 \text{ Hz}$

NOTE: In this case the difference in frequency between each set of peaks is the same and therefore an average determination is not strictly necessary. In fact for 1st order spectra they should be the same. However, in some cases the peak picking programs used will result in small variations, and thus it is necessary to take the trouble to calculate a true average.

To determine the coupling constant of the same multiplet using chemical shift data (δ), calculate the difference in ppm between each peak and average the values. Then multiply the chemical shift by the spectrometer field strength (in this case 60 MHz), in order to convert the value from ppm to Hz:

Chemical shift of peak c - chemical shift of peak d = 3.5452 ppm - 3.4275 ppm = 0.1177 ppm

Chemical shift of peak b - chemical shift of peak c = 3.6628 ppm - 3.5452 ppm = 0.1176 ppm

Chemical shift of peak a - chemical shift of peak b = 3.7805 ppm - 3.6628 ppm = 0.1177 ppm

Average: 0.1176 ppm

Average difference in ppm x frequency of the NMR spectrometer = 0.1176 ppm x 60 MHz = 7.056 Hz

$\therefore J(\text{H-H}) = 7.06 \text{ Hz}$

Exercise 3.7.3.1

(Solution on p. 395.)

Calculate the coupling constant for triplet in the spectrum for chloroethane (Figure 3.114) using the data from Table 3.19.

3.7.3.4 Second-order coupling

When coupled nuclei have similar chemical shifts (more specifically, when $\Delta\nu$ is similar in magnitude to J), *second-order coupling* or *strong coupling* can occur. In its most basic form, second-order coupling results in “roofing” (Figure 3.115). The coupled multiplets point to or lean toward each other, and the effect becomes more noticeable as $\Delta\nu$ decreases. The multiplets also become off-centered with second-order coupling. The midpoint between the peaks no longer corresponds exactly to the chemical shift.

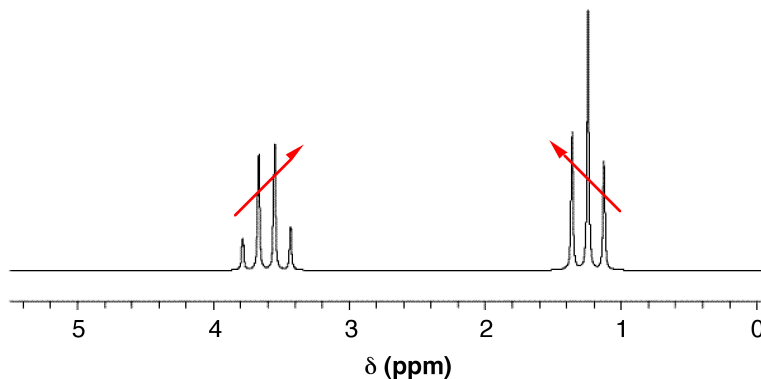


Figure 3.115: Roofing can be seen in the NMR spectrum of chloroethane. Adapted from A. M. Castillo, L. Patiny, and J. Wist, *J. Magn. Reson.*, 2010, **209**, 123.

In more drastic cases of strong coupling (when $\Delta\nu \approx J$), multiplets can merge to create deceptively simple patterns. Or, if more than two spins are involved, entirely new peaks can appear, making it difficult to interpret the spectrum manually. Second-order coupling can often be converted into first-order coupling by using a spectrometer with a higher field strength. This works by altering the $\Delta\nu$ (which is dependent on the field strength), while J (which is independent of the field strength) stays the same.

3.7.3.5 Bibliography

- E. D. Becker, *High Resolution NMR: Theory and Chemical Applications*, 3rd ed., Academic Press, San Diego (2000).
- A. M. Castillo, L. Patiny, and J. Wist, *J. Magn. Reson.*, 2010, **209**, 123.
- H. Günther, *NMR Spectroscopy*, 2nd ed., John Wiley & Sons Inc., New York (1994).
- P. J. Hore, *Nuclear Magnetic Resonance*, Oxford University Press Inc., New York (1995).
- N. E. Jacobsen, *NMR Spectroscopy Explained: Simplified Theory, Applications and Examples for Organic Chemistry and Structural Biology*, John Wiley & Sons Inc., Hoboken, New Jersey (2007).
- J. Keeler, *Understanding NMR Spectroscopy*, John Wiley & Sons Inc., Hoboken, New Jersey (2005).

3.7.4 NMR Spectroscopy of Stereoisomers²²

3.7.4.1 Introduction

Nuclear magnetic resonance (NMR) spectroscopy is a very useful tool used widely in modern organic chemistry. It exploits the differences in the magnetic properties of different nuclei in a molecule to yield information about the chemical environment of the nuclei, and subsequently the molecule, in question. NMR analysis lends itself to scientists more easily than say the more cryptic data achieved from ultraviolet or infrared spectra because the differences in magnetic properties lend themselves to scientists very well. The chemical shifts that are characteristic of different chemical environments and the multiplicity of the peaks fit well with our conception of the way molecules are structured.

Using NMR spectroscopy, we can differentiate between constitutional isomers, stereoisomers, and enantiomers. The later two of these three classifications require close examination of the differences in NMR spectra associated with changes in chemical environment due to symmetry differences; however, the differentiation of constitutional isomers can be easily obtained.

3.7.4.2 Constitutional isomerism

Nuclei both possess charge and spin, or angular momentum, and from basic physics we know that a spinning charge generates a magnetic moment. The specific nature of this magnetic moment is the main concern of NMR spectroscopy.

For proton NMR, the local chemical environment makes different protons in a molecule resonate at different frequencies. This difference in resonance frequencies can be converted into a chemical shift (δ) for each nucleus being studied. Because each chemical environment results in a different chemical shift, one can easily assign peaks in the NMR data to specific functional groups based upon precedent. Precedents for chemical shifts can be found in any number of basic NMR text. For example, Figure 3.116 shows the spectra of ethyl formate and benzyl acetate. In the lower spectra, benzyl acetate, notice peaks at $\delta = 1.3$, 4.2, and 8.0 ppm characteristic of the primary, secondary, and aromatic protons, respectively, present in the molecule. In the spectra of ethyl formate (Figure 3.116b), notice that the number of peaks is the same as that of benzyl acetate (Figure 3.116a); however, the multiplicity of peaks and their shifts is very different.

²²This content is available online at <<http://cnx.org/content/m38355/1.1/>>.

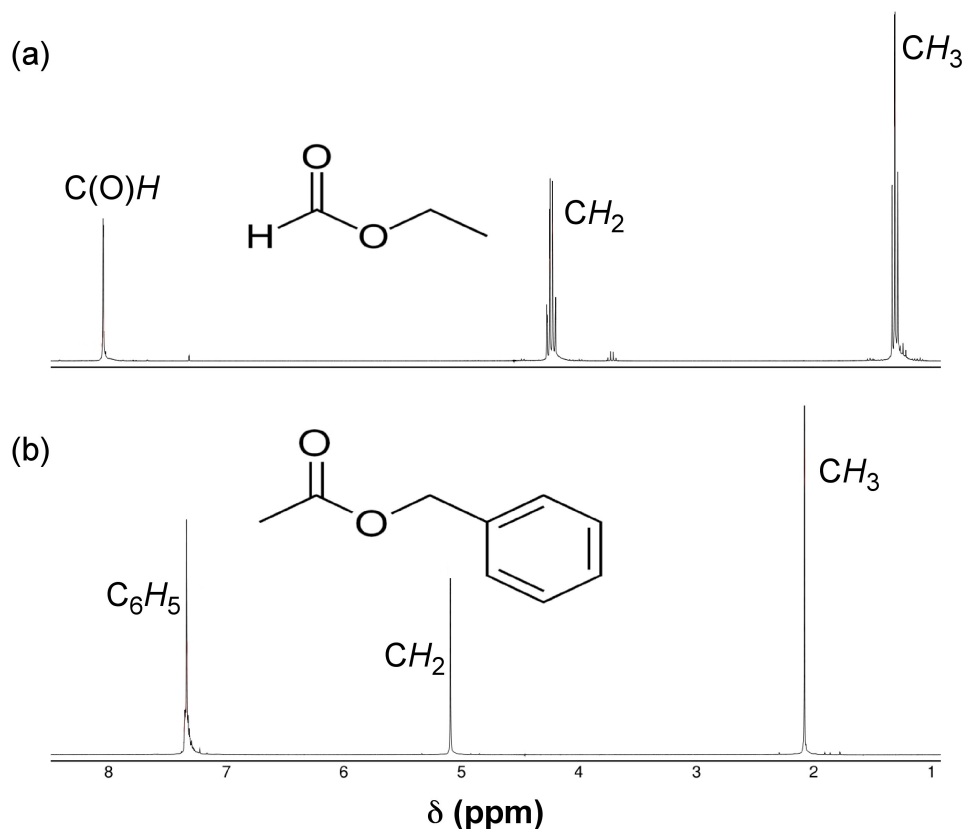


Figure 3.116: ^1H NMR spectra of (a) ethyl formate and (b) benzyl acetate.

The difference between these two spectra is due to geminal spin-spin coupling. Spin-spin coupling is the result of magnetic interaction between individual protons transmitted by the bonding electrons between the protons. This spin-spin coupling results in the peak splitting we see in the NMR data. One of the benefits of NMR spectroscopy is the sensitivity to very slight changes in chemical environment.

3.7.4.3 Stereoisomerism

3.7.4.3.1 Diastereomers

Based on their definition, diastereomers are stereoisomers that are not mirror images of each other and are not superimposable. In general, diastereomers have differing reactivity and physical properties. One common example is the difference between threose and erythrose (Figure 3.117).

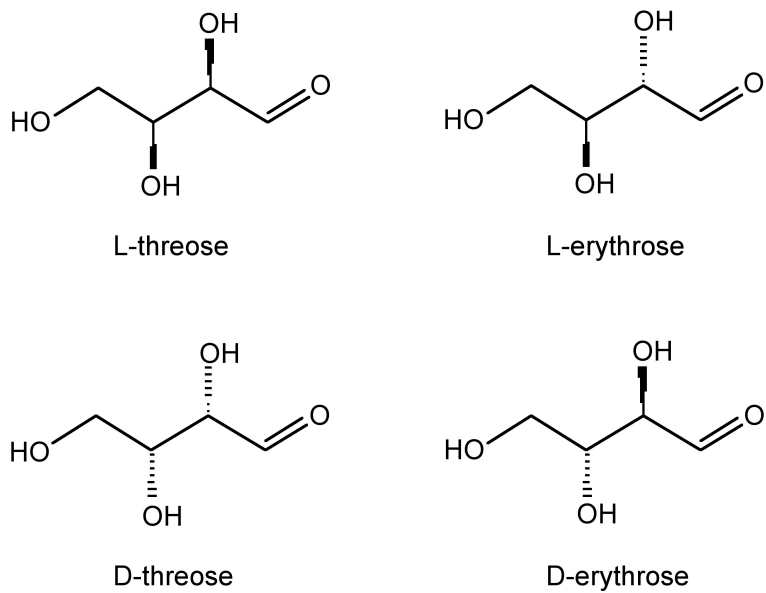


Figure 3.117: The structures of threose and erythrose.

As one can see from Figure 3.117, these chemicals are very similar each having the empirical formula of $C_4H_7O_4$. One may wonder: how are these slight differences in chemical structure represented in NMR? To answer this question, we must look at the Newman projections for a molecule of the general structure (Figure 3.118).

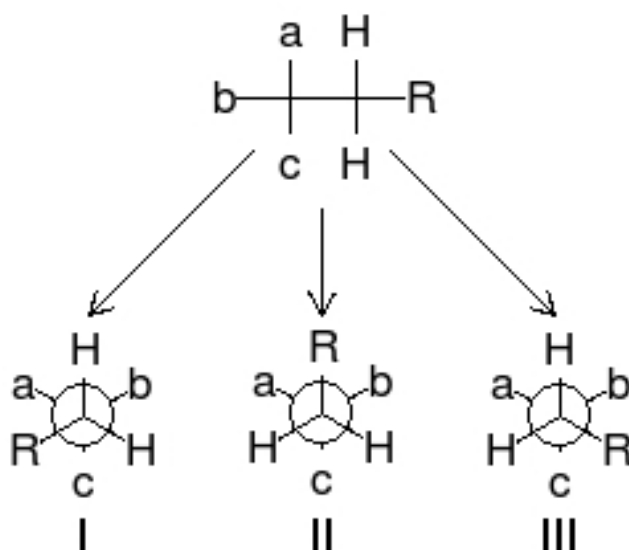


Figure 3.118: Newman projections of a general diastereomer.

One can easily notice that the two protons represented are always located in different chemical environments. This is true because the R group makes the proton resonance frequencies $\nu_1(\text{I}) \neq \nu_2(\text{III})$, $\nu_2(\text{I}) \neq \nu_1(\text{II})$, and $\nu_2(\text{II}) \neq \nu_1(\text{III})$. Thus, diastereomers have different vicinal proton-proton couplings and the resulting chemical shifts can be used to identify the isomeric makeup of the sample.

3.7.4.3.2 Enantiomers

Enantiomers are compounds with a chiral center. In other words, they are non-superimposable mirror images. Unlike diastereomers, the only difference between enantiomers is their interaction with polarized light. Unfortunately, this indistinguishability of racemates includes NMR spectra. Thus, in order to differentiate between enantiomers, we must make use of an optically active solvent also called a chiral derivatizing agent (CDA). The first CDA was (α -methoxy- α -(trifluoromethyl)phenyl)acetic acid (MTPA also known as Mosher's acid) (Figure 3.119).

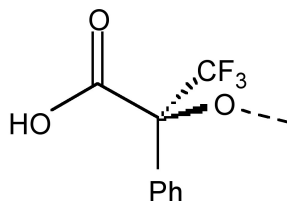


Figure 3.119: The structure of the S-isomer of Mosher's Acid (S-MTPA)

Now, many CDAs exist and are readily available. It should also be noted that CDA development is a current area of active research. In simple terms, one can think of the CDA turning an enantiomeric mixture into a mixture of diastereomeric complexes, producing doublets where each half of the doublet corresponds to each diastereomer, which we already know how to analyze. The resultant peak splitting in the NMR spectra due to diastereomeric interaction can easily determine optical purity. In order to do this, one may simply integrate the peaks corresponding to the different enantiomers thus yielding optical purity of incompletely resolved racemates. One thing of note when performing this experiment is that this interaction between the enantiomeric compounds and the solvent, and thus the magnitude of the splitting, depends upon the asymmetry or chirality of the solvent, the intermolecular interaction between the compound and the solvent, and thus the temperature. Thus, it is helpful to compare the spectra of the enantiomer-CDA mixture with that of the pure enantiomer so that changes in chemical shift can be easily noted.

3.7.4.4 Bibliography

- H. Günther, *NMR Spectroscopy: Basic Principles, Concepts, and Applications in Chemistry*, John Wiley & Sons, Chichester (1996).
- F. A. Bovey, *Nuclear Magnetic Resonance Spectroscopy*, 2nd Ed, Academic, New York (1988).
- S. Braun, H.-O. Kalinowski, S. Berger, *100 and More Basic NMR Experiments: A Practical Course*, VCH, Weinheim (1996).
- A. E. Derome, *Modern NMR Techniques for Chemistry Research*, Pergamon, Oxford (1987).
- J. A. Dale and H. S. Mosher, *J. Am. Chem. Soc.*, 1973, **95**, 512.

3.7.5 Basics of Solid-State NMR²³

3.7.5.1 Introduction

NMR stands for nuclear magnetic resonance and functions as a powerful tool for chemical characterization. Even though NMR is used mainly for liquids and solutions, technology has progressed to where NMR of solids can be obtained with ease. Aptly named as solid state NMR, the expansion of usable phases has invariably increased our ability to identify chemical compounds. The reason behind difficulties using the solid state lie in the fact that solids are never uniform. When put through a standard NMR, line broadening interactions cannot be removed by rapid molecular motions, which results in unwieldy wide lines which provide little to no useful information. The difference is so staggering that lines broaden by hundreds to thousands of hertz as opposed to less than 0.1 Hz in solution when using an $I = 1/2$ spin nucleus.

A process known as magic angle spinning (MAS), where the sample is tilted at a specific angle, is used in order to overcome line broadening interactions and achieve usable peak resolutions. In order to understand

²³This content is available online at <<http://cnx.org/content/m43547/1.1/>>.

solid state NMR, its history, operating chemical and mathematical principles, and distinctions from gas phase/solution NMR will be explained.

3.7.5.2 History

The first notable contribution to what we know today as NMR was Wolfgang Pauli's (Figure 3.120) prediction of nuclear spin in 1926. In 1932 Otto Stern (Figure 3.121) used molecular beams and detected nuclear magnetic moments.



Figure 3.120: Austrian theoretical physicist Wolfgang Ernst Pauli (1900-1958).



Figure 3.121: German physicist Otto Stern (1888 - 1969).

Four years later, Gorter performed the first NMR experiment with lithium fluoride (LiF) and hydrated potassium alum ($\text{K}[\text{Al}(\text{SO}_4)_2] \bullet 12\text{H}_2\text{O}$) at low temperatures. Unfortunately, he was unable to characterize the molecules and the first successful NMR for a solution of water was taken in 1945 by Felix Bloch (Figure 3.122). In the same year, Edward Mills Purcell (Figure 3.123) managed the first successful NMR for the solid paraffin. Continuing their research, Bloch obtained the ^1H NMR of ethanol and Purcell obtained that of paraffin in 1949. In the same year, the chemical significance of chemical shifts was discovered. Finally, high resolution solid state NMR was made possible in 1958 by the discovery of magic angle spinning.

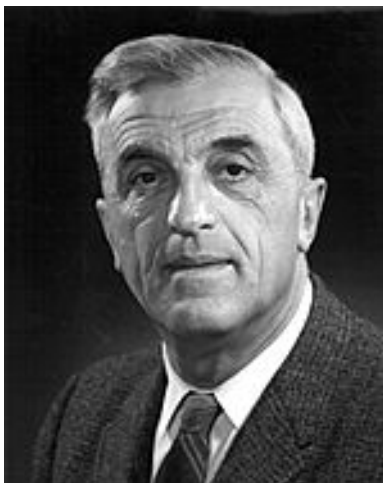


Figure 3.122: Swiss physicist Felix Bloch (1905-1983).

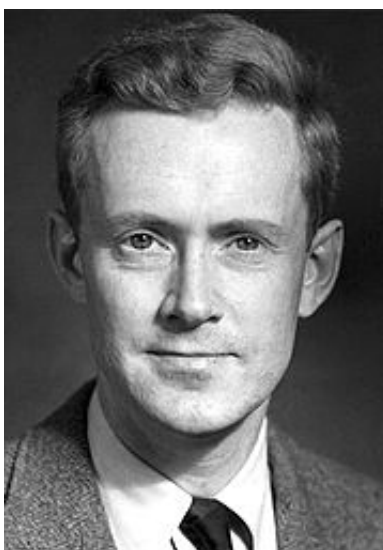


Figure 3.123: American physicist Edward Mills Purcell (1912-1997).

3.7.5.3 How it works: from machine to graph

NMR spectroscopy works by measuring the nuclear shielding, which can also be seen as the electron density, of a particular element. Nuclear shielding is affected by the chemical environment, as different neighboring

atoms will have different effects on nuclear shielding, as electronegative atoms will tend to decrease shielding and vice versa. NMR requires the elements analyzed to have a spin state greater than zero. Commonly used elements are ^1H , ^{13}C , and ^{29}Si . Once inside the NMR machine, the presence of a magnetic field splits the spin states (Figure 3.124).

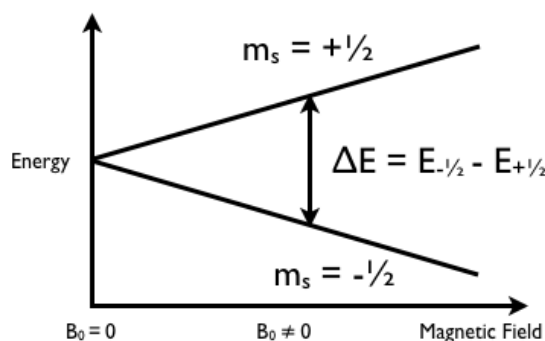


Figure 3.124: Spin state splitting as a function of applied magnetic field.

From (Figure 3.124) we see that a spin state of $1/2$ is split into two spin states. As spin state value increases, so does the number of spin states. A spin of 1 will have three spin states, $3/2$ will have four spin states, and so on. However, higher spin states increases the difficulty to accurately read NMR results due to confounding peaks and decreased resolution, so spin states of $1/2$ are generally preferred. The E, or radiofrequency shown in (Figure 3.124) can be described by (3.11), where μ is the magnetic moment, a property intrinsic to each particular element. This constant can be derived from (3.12), where γ is the gyromagnetic ratio, another element dependent quantity, h is Planck's constant, and I is the spin.

$$E = \mu B_0 H_0 \quad (3.11)$$

$$\mu = \gamma h(I(I+1))^{1/2} \quad (3.12)$$

(3.11) can have E substituted for $h\nu$, leading to (3.13), which can solve for the NMR resonance frequency (ν).

$$h\nu = \mu B_0 H_0 \quad (3.13)$$

Using the frequency (ν), the δ , or expected chemical shift may be computed using (3.14).

$$\delta = \frac{(\nu_{\text{observed}} - \nu_{\text{reference}})}{\nu_{\text{spectrometer}}} \quad (3.14)$$

Delta (δ) is observed in ppm and gives the distance from a set reference. Delta is directly related to the chemical environment of the particular atom. For a low field, or high delta, an atom is in an environment which produces induces less shielding than in a high field, or low delta.

3.7.5.4 NMR instrument

An NMR can be divided into three main components: the workstation computer where one operates the NMR instrument, the NMR spectrometer console, and the NMR magnet. A standard sample is inserted through the bore tube and pneumatically lowered into the magnet and NMR probe (Figure 3.125).

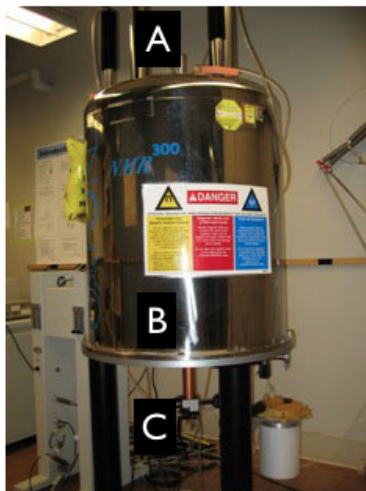


Figure 3.125: Standard NMR instrument, with main components labeled: (A) bore tube, (B) outer magnet shell, (C) NMR probe.

The first layer inside the NMR (Figure 3.126) is the liquid nitrogen jacket. Normally, this space is filled with liquid nitrogen at 77 K. The liquid nitrogen reservoir space is mostly above the magnet so that it can act as a less expensive refrigerant to block infrared radiation from reaching the liquid helium jacket.

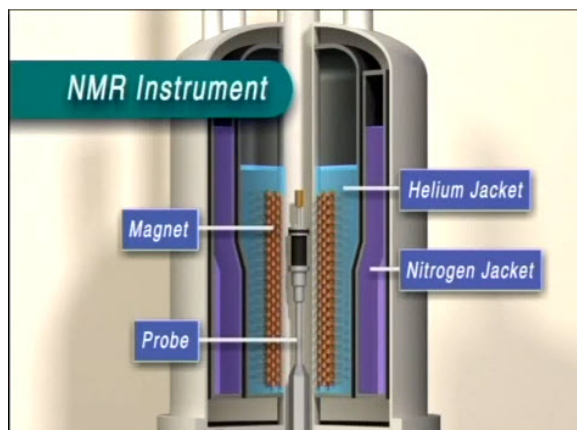


Figure 3.126: Diagram of the main layers inside an NMR machine.

The layer following the liquid nitrogen jacket is a 20 K radiation shield made of aluminum wrapped with alternating layers of aluminum foil and open weave gauze. Its purpose is to block infrared radiation which the 77 K liquid nitrogen vessel was unable to eliminate, which increases the ability for liquid helium to remain in the liquid phase due to its very low boiling point. The liquid helium vessel itself, the next layer, is made of stainless steel wrapped in a single layer of aluminum foil, acting once again as an infrared radiation shield. It is about 1.6 mm thick and kept at 4.2 K.

Inside the vessel and around the magnet is the aluminum baffle, which acts as another degree of infrared radiation protection as well as a layer of protection for the superconducting magnet from liquid helium reservoir fluctuations, especially during liquid helium refills. The significance is that superconducting magnets at low fields are not fully submerged in liquid helium, but higher field superconducting magnets must maintain the superconducting solenoid fully immersed in liquid helium. The vapor above the liquid itself is actually enough to maintain superconductivity of most magnets, but if it reaches a temperature above 10 K, the magnet quenches. During a quench, the solenoid exceeds its critical temperature for superconductivity and becomes resistive, generating heat. This heat, in turn, boils off the liquid helium. Therefore, a small opening at the very base of the baffle exists as a path for the liquid helium to reach the magnet surface so that during refills the magnet is protected from accidental quenching.

3.7.5.5 Problems with solid state NMR

The most notable difference between solid samples and solution/gas in terms of NMR spectroscopy is that molecules in solution rotate rapidly while those in a solid are fixed in a lattice. Different peak readings will be produced depending on how the molecules are oriented in the magnetic field because chemical shielding depends upon the orientation of a molecule, causing chemical shift anisotropy. Therefore, the effect of chemical shielding also depends upon the orientation of the molecule with respect to the spectrometer. These counteracting forces are balanced out in gases and solutions because of their randomized molecular movement, but become a serious issue with fixed molecules observed in solid samples. If the chemical shielding isn't determined accurately, neither will the chemical shifts (δ).

Another issue with solid samples are dipolar interactions which can be very large in solid samples causing linewidths of tens to hundreds of kilohertz to be generated. Dipolar interactions are tensor quantities, which demonstrate values dependent on the orientation and placement of a molecule in reference to its surroundings. Once again the issue goes back to the lattice structure of solids, which are in a fixed location.

Even though the molecules are fixed, this does not mean that nuclei are evenly spread apart. Closer nuclei display greater dipolar interactions and vice versa, creating the noise seen in spectra of NMR not adapted for solid samples. Dipolar interactions are averaged out in solution states because of randomized movement. Spin state repulsions are averaged out by molecular motion of solutions and gases. However, in solid state, these interactions are not averaged and become a third source of line broadening.

3.7.5.5.1 Magic angle spinning

In order to counteract chemical shift anisotropy and dipolar interactions, magic angle spinning was developed. As discussed above, describing dipolar splitting and chemical shift anisotropy interactions respectively, it becomes evident that both depend on the geometric factor ($3\cos^2\theta-1$).

$$\text{Dipolar splitting} = C(\mu_0/8\pi)(\gamma_a\gamma_x/r_{ax}^2)(3\cos^2\theta_{iz}-1) \quad (3.15)$$

$$\sigma_{zz} = \bar{\sigma} + 1/3\Sigma\sigma_{ii}(3\cos^2\theta_{iz}-1) \quad (3.16)$$

If this factor is decreased to 0, then line broadening due to chemical shift anisotropy and dipolar interactions will disappear. Therefore, solid samples are rotated at an angle of 54.74° , effectively allowing solid samples to behave similarly to solutions/gases in NMR spectroscopy. Standard spinning rates range from 12 kHz to an upper limit of 35 kHz, where higher spin rates are necessary to remove higher intermolecular interactions.

3.7.5.6 Application of solid state NMR

The development of solid state NMR is a technique necessary to understand and classify compounds that would not work well in solutions, such as powders and complex proteins, or study crystals too small for a different characterization method.

Solid state NMR gives information about local environment of silicon, aluminum, phosphorus, etc. in the structures, and is therefore an important tool in determining structure of molecular sieves. The main issue frequently encountered is that crystals large enough for X-Ray crystallography cannot be grown, so NMR is used since it determines the local environments of these elements. Additionally, by using ^{13}C and ^{15}N , solid state NMR helps study amyloid fibrils, filamentous insoluble protein aggregates related to neurodegenerative diseases such as Alzheimer's disease, type II diabetes, Huntington's disease, and prion diseases.

3.7.5.7 Bibliography

- J. W. Akitt, *NMR and Chemistry*, 3rd Edn., Chapman & Hall, London (1992).
- A. R. Grimmer and B. Blümich, *Introduction to Solid-State NMR*, Springer-Verlag, Berlin(1994).
- J. A. Iggo, *NMR Spectroscopy in Inorganic Chemistry*, Oxford University Press, New York (1999).
- J. C. C. Chan, *Top. Curr. Chem.*, 2011, **306**, 47.
- R. Freeman, *Chem Heterocyc Compd*, 1995, **31**, 1004-1005.
- Jeol USA, *JEOL Delta-GSX 270 NMR Magnet Destruction*, <<http://www.jeolusa.com>>
- University of Pittsburgh, *Magnet Safety*, <<http://www.ehs.pitt.edu/assets/docs/magnet-safety.pdf>>, 2008, (accessed 15 February 2012).

3.7.6 Lanthanide Shift Reagents²⁴

3.7.6.1 Introduction

Nuclear magnetic resonance spectroscopy (NMR) is the most powerful tool for organic and organometallic compound determination. Even structures can be determined just using this technique. In general NMR

²⁴This content is available online at <<http://cnx.org/content/m43580/1.1/>>.

gives information about the number of magnetically distinct atoms of the specific nuclei under study, as well as information regarding the nature of the immediate environment surrounding each nuclei. Because hydrogen and carbon are the major components of organic and organometallic compounds, proton (^1H) NMR and carbon-13 (^{13}C) NMR are the most useful nuclei to observe.

Not all the protons experience resonance at the same frequency in a ^1H NMR, and thus it is possible to differentiate between them. The diversity is due to the existence of a different electronic environment around chemically different nuclei. Under an external magnetic field (B_0), the electrons in the valence shell are affected; they start to circulate generating a magnetic field, which is apposite to the applied magnetic field. This effect is called diamagnetic shielding or diamagnetic anisotropy (Figure 3.127).

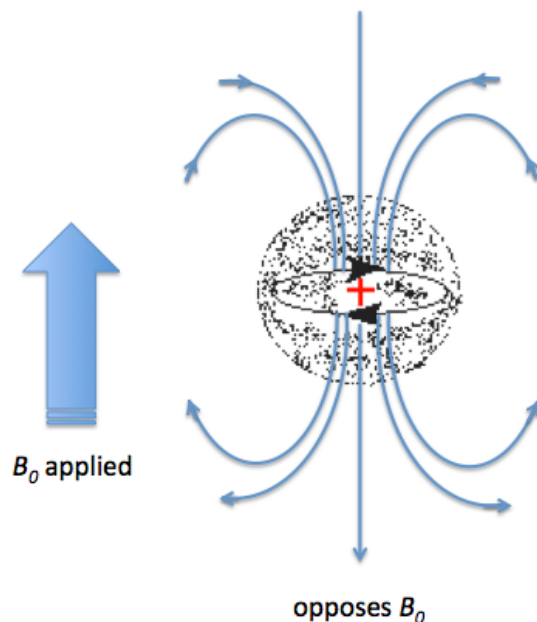


Figure 3.127: Schematic representation of diamagnetic anisotropy. Adapted from D. L. Pavia, G. M. Lampman, and G. S. Kriz, *Introduction to Spectroscopy*, 3th Ed., Thomson Learning, Tampa, FL, (2011).

The greater the electron density around one specific nucleus, the greater will be the induced field that opposes the applied field, and this will result in a different resonance frequency. The identification of protons sounds simple, however, the NMR technique has a relatively low sensitivity of proton chemical shifts to changes in the chemical and stereochemical environment; as a consequence the resonance of chemically similar proton overlap. There are several methods that have been used to resolve this problem, such as: the use of higher frequency spectrometers or by the use of shift reagents as aromatic solvents or lanthanide complexes. The main issue with high frequency spectrometers is that they are very expensive, which reduces the number of institutions that can have access to them. In contrast, shift reagents work by reducing the equivalence of nuclei by altering their magnetic environment, and can be used on any NMR instrument. The simplest shift reagent is the one of different solvents, however problems with some solvents is that they can react with the compound under study, and also that these solvents usually just alter the magnetic environment of a small part of the molecule. Consequently, although there are several methods, most of the

work has been done with lanthanide complexes.

3.7.6.2 The history of lanthanide shift reagents

The first significant induced chemical shift using paramagnetic ions was reported in 1969 by Conrad Hinckley (Figure 3.128), where he used bispyridine adduct of tris(2,2,6,6-tetramethylhepta-3,5-dionato)europium(III) ($\text{Eu}(\text{tmhd})_3$), better known as $\text{Eu}(\text{dpm})_3$, where dpm is the abbreviation of dipivaloyl- methanato, the chemical structure is shown in Figure 3.129. Hinckley used $\text{Eu}(\text{tmhd})_3$ on the ^1H NMR spectrum of cholesterol from 347 – 2 Hz. The development of this new chemical method to improve the resolution of the NMR spectrum was the stepping-stone for the work of Jeremy Sanders and Dudley Williams, Figure 3.130 and Figure 3.131 respectively. They observed a significant increase in the magnitude of the induced shift after using just the lanthanide chelate without the pyridine complex. Suggesting that the pyridine donor ligands are in competition for the active sites of the lanthanide complex. The efficiency of $\text{Eu}(\text{tmhd})_3$ as a shift reagent was published by Sanders and Williams in 1970, where they showed a significant difference in the ^1H NMR spectrum of n-pentanol using the shift reagent, see Figure 3.132.



Figure 3.128: Chemist Conrad Hinckley, Emeritus professor in Southern Illinois University..

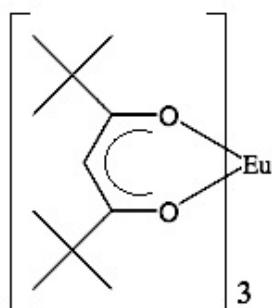


Figure 3.129: Chemical structure of $\text{Eu}(\text{tmhd})_3$.



Figure 3.130: British chemist Jeremy Keith Morris Sanders.



Figure 3.131: British chemist Dudley Williams (1937-2010).

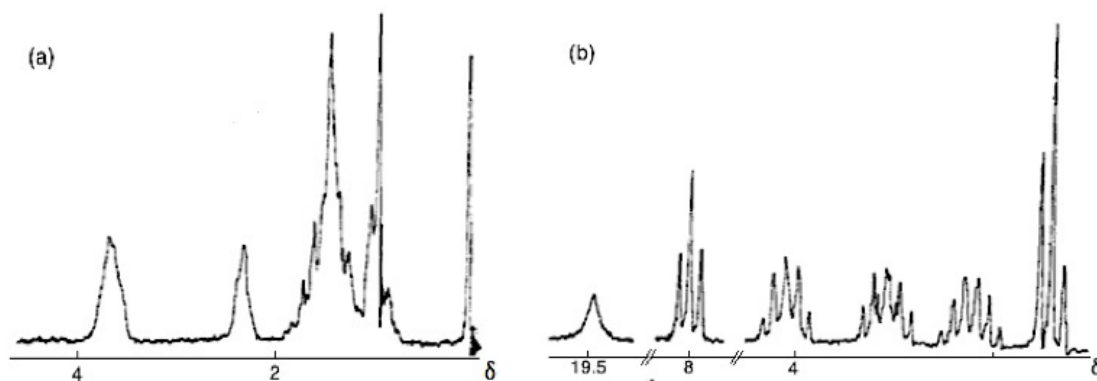


Figure 3.132: ¹H NMR spectra of n-pentanol, (a) without the presence of lanthanide reagents and (b) in the presence of the lanthanide reagent Eu(tmhd)₃. Adapted from *Chem Reviews*, 1973, **73**, 553. Copyright: American Chemical Society 1973.

Analyzing the spectra in Figure 3.132 it is easy to see that with the use of Eu(tmhd)₃ there is any overlap between peaks. Instead, the multiplets of each proton are perfectly clear. After these two publications the potential of lanthanide as shift reagents for NMR studies became a popular topic. Other example is the fluorinate version of Eu(dpm)₃; (*tris*(7,7-dimethyl-1,1,2,2,3,3,3-heptafluoroocta-7,7-dimethyl-4,6-dionato)europium(III), best known as Eu(fod)₃, which was synthesized in 1971 by Rondeau and Sievers.

This LSR presents better solubility and greater Lewis acid character, the chemical structure is show in Figure 3.133.

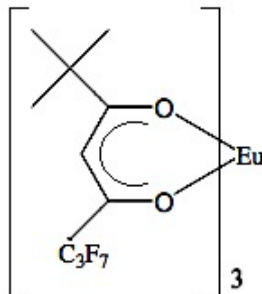


Figure 3.133: Chemical structure of (*tris*(7,7,-dimethyl-1,1,2,2,3,3-heptafluoroocta-7,7-dimethyl-4,6-dionato)europium(III)).

3.7.6.3 Mechanism of inducement of chemical shift

Lanthanide atoms are Lewis acids, and because of that, they have the ability to cause chemical shift by the interaction with the basic sites in the molecules. Lanthanide metals are especially effective over other metals because there is a significant delocalization of the unpaired *f* electrons onto the substrate as a consequence of unpaired electrons in the *f* shell of the lanthanide. The lanthanide metal in the complexes interacts with the relatively basic lone pair of electrons of aldehydes, alcohols, ketones, amines and other functional groups within the molecule that have a relative basic lone pair of electrons, resulting in a NMR spectral simplification.

There are two possible mechanisms by which a shift can occur: shifts by contact and shifts by pseudocontact. The first one is a result of the transfer of electron spin density via covalent bond formation from the lanthanide metal ion to the associated nuclei. While the magnetic effects of the unpaired electron magnetic moment causes the pseudocontact shift. Lanthanide complexes give shifts primarily by the pseudocontact mechanism. Under this mechanism, there are several factors that influence the shift of a specific NMR peak. The principal factor is the distance between the metal ion and the proton; the shorter the distance, the greater the shift obtained. On the other hand, the direction of the shift depends on the lanthanide complex used. The complexes that produce a shift to a lower field (downfield) are the ones containing erbium, europium, thulium and ytterbium, while complexes with cerium, neodymium, holmium, praseodymium, samarium and terbium, shift resonances to higher field. Figure 6 shows the difference between an NMR spectrum without the use of shift reagent versus the same spectrum in the present of a europium complex (downfield shift) and a praseodymium complex (high-field shift).

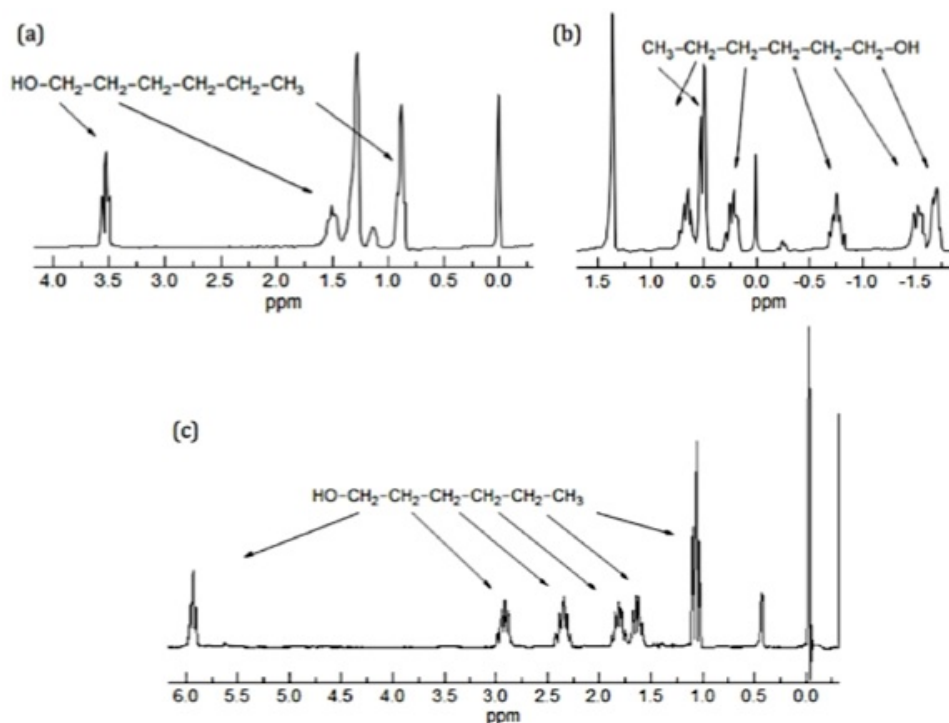


Figure 3.134: (a) ^1H NMR spectrum of n-hexanol without the present of shift reagents. (b) ^1H NMR spectrum of n-hexanol in present of 14% $\text{Pr}(\text{fod})_3$ and the third spectrum (c) is the ^1H NMR spectrum of n-hexanol in the present of 6.5% $\text{Eu}(\text{fod})_3$. Adapted from <http://www.chem.wisc.edu/areas/reich/nmr/08-tech-07-lis.htm>²⁵

Linewidth broadening is not desired because of loss of resolution, and lanthanide complexes unfortunately contribute extremely to this effect when they are used in high concentrations due to their mechanism that shortens the relaxation times (T_2), which in turn increases the bandwidth. However europium and praseodymium are an extraordinary exception giving a very low shift broadening, 0.003 and 0.005 Hz/Hz respectively. Europium specially is the most used lanthanide as shift reagent because of its inefficient nuclear spin-lattice ratio properties. It has low angular momentum quantum numbers and a diamagnetic $7F_0$ ground state. These two properties contribute to a very small separation of the highest and lowest occupied metal orbitals leading to an inefficient relaxation and a very little broadening in the NMR spectra. The excited $7F_1$ state will then contribute to the pseudocontact shift.

We have mentioned above that lanthanide complexes have a mechanism that influences relaxation times, and this is certainly because paramagnetic ions have an influence in both: chemical shifts and relaxation rates. The relaxation times are of great significant because they depend on the width of a specific resonance (peak). Changes in relaxation time could also be related with the geometry of the complex.

3.7.6.4 Measuring the shift

The easiest and more practical way to measure the lanthanide-induced shift (LIS) is to add aliquots of the lanthanide shift reagent (LSR or $\Delta\nu$) to the sample that has the compound of interest (substrate), and take

²⁵<http://www.chem.wisc.edu/areas/reich/nmr/08-tech-07-lis.htm>

an NMR spectra after each addition. Because the shift of each proton will change after each addition of the LSR to lower or upper field, the LIS can be measured. With the data collected, a plot of the LIS against the ratio of LSR: substrate will generate a straight line where the slope is representative of the compound that is being studied. The identification of the compound by the use of chiral lanthanide shift reagents can be so precise that it is possible to estimate the composition of enantiomers in the solution under study, see Figure 3.135.

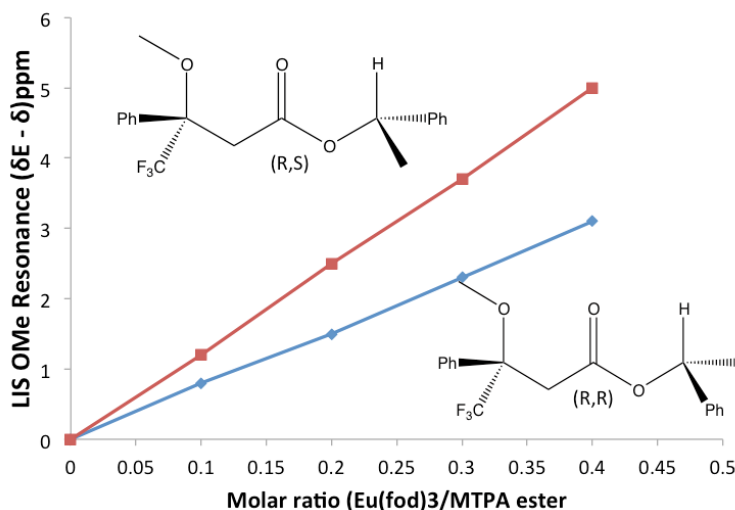


Figure 3.135: Lanthanide induced shift of methoxyl proton resonance versus molar ratio of Eu(fod)_3 , for the diastereomeric MTPA esters. δ is the normal chemical shift and δ_E is the chemical shift in ppm for the OMe signal in the presence of a specified molar ratio of Eu(fod)_3 , in CCl_4 as solvent. Adapted from S. Yamaguchi, F. Yasuhara and K. Kabuto, *Tetrahedron*, 1976, **32**, 1363.

Now, what is the mechanism that is actually happening between the LSR and the compound under study? The LSR is a metal complex of six coordinate sites. The LSR, in presence of substrate that contains heteroatoms with Lewis basicity character, expands its coordination sites in solution in order to accept additional ligands. An equilibrium mixture is formed between the substrate and the LSR. (3.17) and (3.18) show the equilibrium, where L is LSR, S is the substrate, and LS is the concentration of the complex formed in solution.



The abundance of these species depends on K_1 and K_2 , which are the binding constant. The binding constant is a special case of equilibrium constant, but it refers with the binding and unbinding mechanism of two species. In most of the cases like, K_2 is assumed to be negligible and therefore just the first complex $[\text{LS}]$ is assumed to be formed. The equilibrium between $\text{L} + \text{S}$ and $[\text{LS}]$ in solution is faster than the NMR timescale, consequently a single average signal will be recorded for each nucleus.

3.7.6.5 Determination of enantiomeric purity

Besides the great potential of lanthanide shift reagents to improve the resolution of NMR spectrums, these complexes also have been used to identify enantiomeric mixtures in solution. To make this possible the substrate must meet certain properties. The first one is that the organic compounds in the enantiomeric composition must to have a hard organic base as functional group. The shift reagents are not effective with most of the soft bases. Though hundreds of chelates have been synthesized after $\text{Eu}(\text{dcm})_3$, this one is the LSR that resulted in the most effective reagent for the resolution of enantiotopic resonances. Basically if you take an NMR of an enantiomeric mixture sample, a big variety of peaks will appear and the hard part is to identify which of those peaks correspond to which specific enantiomer. The differences in chemical shifts observed for enantiomeric mixtures in solution containing LSR might arise from at least two sources: the equilibrium constants of the formation of the possible diastereometric complexes between the substrate and the LSR, and the geometries of these complexes, which might be distinct. The enantiomeric shift differences sometimes are defined as $\Delta\Delta\delta$.

In solution the exchange between substrate coordinated to the europium ion and the free substrate in solution is very fast. To be sure that the europium complexes are binding with one or two substrate molecules, an excess of substrate is usually added.

3.7.6.6 Biography

- L. G. Wade, Jr., *Organic Chemistry*, 4th edn., Upper Saddle River, New Jersey (2006).
- D. L. Pavia, G. M. Lampman, and G. S. Kriz, *Introduction to Spectroscopy*, 3th edn., Bellingham, WA (2001).
- J. B. Lambert and E. P. Mazzola, *Nuclear Magnetic Resonance Spectroscopy*, Upper Saddle River, New Jersey (2004).
- C. C. Hinckley, *J. Am. Chem. Soc.*, 1969, **91**, 5160.
- J. K. M. Sanders and D. H. Williams, *J. Am. Chem. Soc.*, 1971, **93**, 1641.
- A. F. Cockerill, G. L. O. Davies, R. C. Harden, and D. M. Rackham, *Chem. Rev.*, 1973, **73**, 553.
- B. C. Mayor, *J. Am. Chem. Soc.*, 1969, **91**, 49.
- S. Yamaguchi, F. Yasuhara, and K. Kabuto, *Tetrahedron*, 1976, **32**, 1363.

3.8 EPR Spectroscopy

3.8.1 EPR Spectroscopy: An Overview²⁶

3.8.1.1 Basic principles for EPR spectroscopy

Electron paramagnetic resonance spectroscopy (EPR) is a powerful tool for investigating paramagnetic species, including organic radicals, inorganic radicals, and triplet states. The basic principles behind EPR are very similar to the more ubiquitous nuclear magnetic resonance spectroscopy (NMR), except that EPR focuses on the interaction of an external magnetic field with the unpaired electron(s) in a molecule, rather than the nuclei of individual atoms. EPR has been used to investigate kinetics, mechanisms, and structures of paramagnetic species and along with general chemistry and physics, has applications in biochemistry, polymer science, and geosciences.

The degeneracy of the electron spin states is lifted when an unpaired electron is placed in a magnetic field, creating two spin states, $m_s = \pm \frac{1}{2}$, where $m_s = -\frac{1}{2}$, the lower energy state, is aligned with the magnetic field. The spin state on the electron can flip when electromagnetic radiation is applied. In the case of electron spin transitions, this corresponds to radiation in the microwave range.

The energy difference between the two spin states is given by the equation

$$\Delta E = E_+ - E_- = h\nu = g\beta B$$

²⁶This content is available online at <<http://cnx.org/content/m22370/1.3/>>.

where h is Planck's constant ($6.626 \times 10^{-34} \text{ J s}^{-1}$), ν is the frequency of radiation, $\hbar$ is the Bohr magneton ($9.274 \times 10^{-24} \text{ J T}^{-1}$), B is the strength of the magnetic field in Tesla, and g is known as the g -factor. The g -factor is a unitless measurement of the intrinsic magnetic moment of the electron, and its value for a free electron is 2.0023. The value of g can vary, however, and can be calculated by rearrangement of the above equation, i.e.,

$$g = h\nu / \hbar B$$

using the magnetic field and the frequency of the spectrometer. Since h , ν , and $\hbar$ should not change during an experiment, g values decrease as B increases. The concept of g can be roughly equated to that of chemical shift in NMR.

3.8.1.2 Instrumentation

EPR spectroscopy can be carried out by either 1) varying the magnetic field and holding the frequency constant or 2) varying the frequency and holding the magnetic field constant (as is the case for NMR spectroscopy). Commercial EPR spectrometers typically vary the magnetic field and holding the frequency constant, opposite of NMR spectrometers. The majority of EPR spectrometers are in the range of 8-10 GHz (X-band), though there are spectrometers which work at lower and higher fields: 1-2 GHz (L-band) and 2-4 GHz (S-band), 35 GHz (Q-band) and 95 GHz (W-band).

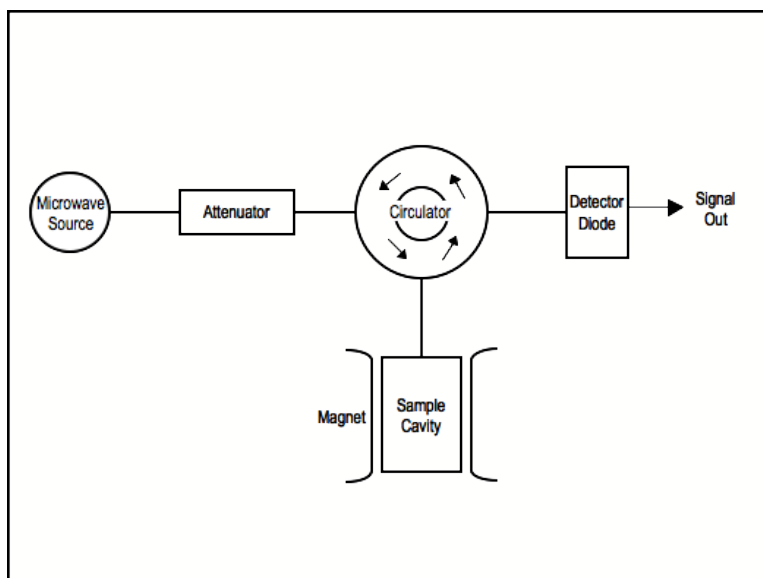


Figure 3.136: Block diagram of a typical EPR spectrometer.

EPR spectrometers work by generating microwaves from a source (typically a klystron), sending them through an attenuator, and passing them on to the sample, which is located in a microwave cavity (Figure 3.136). Microwaves reflected back from the cavity are routed to the detector diode, and the signal comes out as a decrease in current at the detector analogous to absorption of microwaves by the sample.

Samples for EPR can be gases, single crystals, solutions, powders, and frozen solutions. For solutions, solvents with high dielectric constants are not advisable, as they will absorb microwaves. For frozen solutions, solvents that will form a glass when frozen are preferable. Good glasses are formed from solvents with low

symmetry and solvents that do not hydrogen bond. Drago provides an extensive list of solvents that form good glasses.

EPR spectra are generally presented as the first derivative of the absorption spectra for ease of interpretation. An example is given in Figure 3.137.

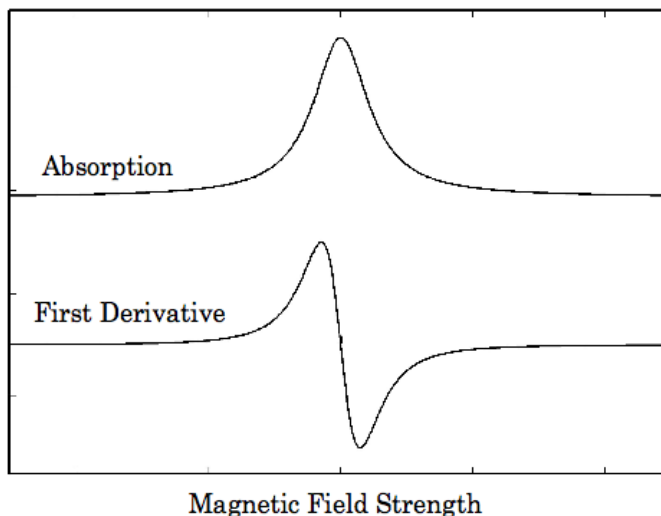


Figure 3.137: Example of first and second derivative EPR spectrum.

Magnetic field strength is generally reported in units of Gauss or mTesla. Often EPR spectra are very complicated, and analysis of spectra through the use of computer programs is usual. There are computer programs that will predict the EPR spectra of compounds with the input of a few parameters.

3.8.1.3 Factors that affect EPR spectra

3.8.1.3.1 Hyperfine coupling

Hyperfine coupling in EPR is analogous to spin-spin coupling in NMR. There are two kinds of hyperfine coupling: 1) coupling of the electron magnetic moment to the magnetic moment of its own nucleus; and 2) coupling of the electron to a nucleus of a different atom, called super hyperfine splitting. Both types of hyperfine coupling cause a splitting of the spectral lines with intensities following Pascal's triangle for $I = 1/2$ nuclei, similar to J-coupling in NMR. A simulated spectrum of the methyl radical is shown in Figure 3.138. The line is split equally by the three hydrogens giving rise to four lines of intensity 1:3:3:1 with hyperfine coupling constant a .

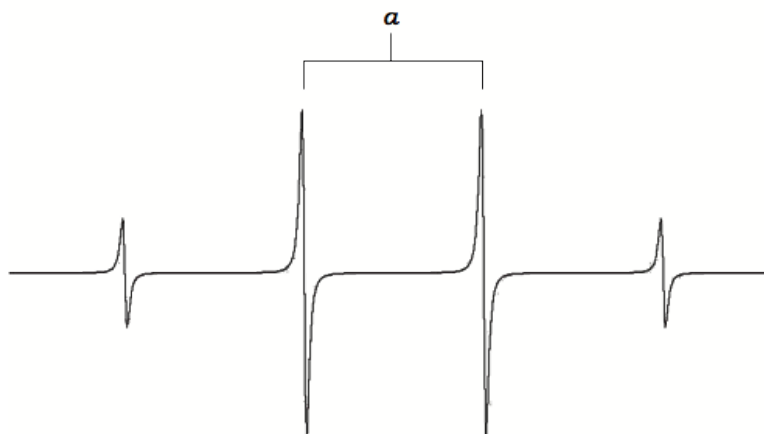


Figure 3.138: Simulated spectrum of CH_3 radical with hyperfine coupling constant a .

The hyperfine splitting constant, known as a , can be determined by measuring the distance between each of the hyperfine lines. This value can be converted into Hz (A) using the g value in the equation:

$$hA = g$$

In the specific case of Cu(II), the nuclear spin of Cu is $I = 3/2$, so the hyperfine splitting would result in four lines of intensity 1:1:1:1. Similarly, super hyperfine splitting of Cu(II) ligated to four symmetric $I = 1$ nuclei, such as ^{14}N , would yield nine lines with intensities would be 1:8:28:56:70:56:28:8:1.

3.8.1.3.2 Anisotropy

The g factor of many paramagnetic species, including Cu(II), is anisotropic, meaning that it depends on its orientation in the magnetic field. The g factor for anisotropic species breaks down generally into three values of g following a Cartesian coordinate system which is symmetric along the diagonal: g_x , g_y , and g_z . There are four limits to this system:

- i) When $g_x = g_y = g_z$ the spectrum is considered to be isotropic, and is not dependent on orientation in the magnetic field.
- ii) When $g_x = g_y > g_z$ the spectrum is said to be axial, and is elongated along the z -axis. The two equivalent g values are known as $g_{\perp}$ while the singular value is known as $g_{\parallel}$. It exhibits a small peak at low field and a large peak at high field.
- iii) When $g_x = g_y < g_z$ the spectrum is also said to be axial, but is shortened in the xy plane. It exhibits a large peak at low field and a small peak at high field.
- iv) When $g_x \neq g_y \neq g_z$ the spectrum is said to be rhombic, and shows three large peaks corresponding to the different components of g .

Condition ii corresponds to Cu(II) in a square planar geometry with the unpaired electron in the $d_{x^2-y^2}$ orbital. Where there is also hyperfine splitting involved, g is defined as being the weighted average of the lines.

3.8.1.4 Bibliography

- R. S. Drago, *Physical Methods for Chemists*. 2nd edition, Saunders College Publishing, Mexico (1992).

- G. Palmer, In *Physical Methods in Bioinorganic Chemistry Spectroscopy and Magnetism*. Ed. L. Que, University Science Books, Sausalito, CA (2000).
- P. H. Rieger, *Electron Spin Resonance: Analysis and Interpretation*. Royal Society of Chemistry, Cambridge, UK, (2007).
- J. Weil, J. Bolton, and J. Wertz, *Electron Paramagnetic Resonance: Elemental Theory and Practical Applications*, John Wiley and Sons, New York (1994).

3.8.2 Electron Paramagnetic Resonance Spectroscopy of Copper(II) Compounds²⁷

3.8.2.1 Copper(II) Compounds

Copper compounds play a valuable role in both synthetic and biological chemistry. Copper catalyzes a vast array of reactions, primarily oxidation-reduction reactions which make use of the Cu(I)/Cu(II) redox cycle. Copper is found in the active site of many enzymes and proteins, including the oxygen carrying proteins called hemocyanins.

Common oxidation states of copper include the less stable copper(I) state, Cu^+ ; and the more stable copper(II) state, Cu^{2+} . Copper (I) has a d^{10} electronic configuration with no unpaired electrons, making it undetectable by EPR. The d^9 configuration of Cu^{2+} means that its compounds are paramagnetic making EPR of Cu(II) containing species a useful tool for both structural and mechanistic studies. Two literature examples of how EPR can provide insight into the mechanisms of reactivity of Cu(II) are discussed herein.

Copper (II) centers typically have tetrahedral, or axially elongated octahedral geometry. Their spectra are anisotropic and generally give signals of the axial or orthorhombic type. From EPR spectra of copper (II) compounds, the coordination geometry can be determined. An example of a typical powder Cu(II) spectrum is shown in Figure 3.139.

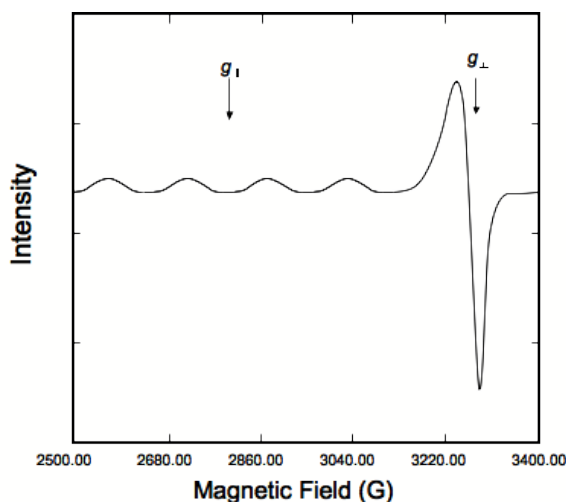


Figure 3.139: Typical axial EPR spectrum for a Cu(II) compound.

²⁷This content is available online at <<http://cnx.org/content/m22507/1.2/>>.

The spectrum above shows four absorption-like peaks corresponding to $g_{[U+2016]}$ indicating coordination to four identical atoms, most likely nitrogen. There is also an asymmetric derivative peak corresponding to $g_{\perp}$ at higher field indicating elongation along the z axis.

3.8.2.1.1 Determination of an intermediate

The reactivity and mechanism of Cu(II)-peroxy systems was investigated by studying the decomposition of the Cu(II) complex **1** with EPR as well as UV-Vis and Raman spectroscopy. The structure (Figure 3.140) and EPR spectrum Figure 3.141 of **1** are given. It was postulated that decomposition of **1** may go through intermediates LCu(II)OOH , $\text{LCu(II)OO}\bullet$, or $\text{LCu(II)O}\bullet$ where L = ligand.

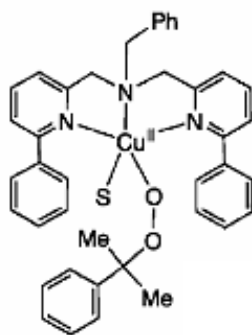


Figure 3.140: Structure of **1**, Cu(II) compound under investigation S = CH_3CN

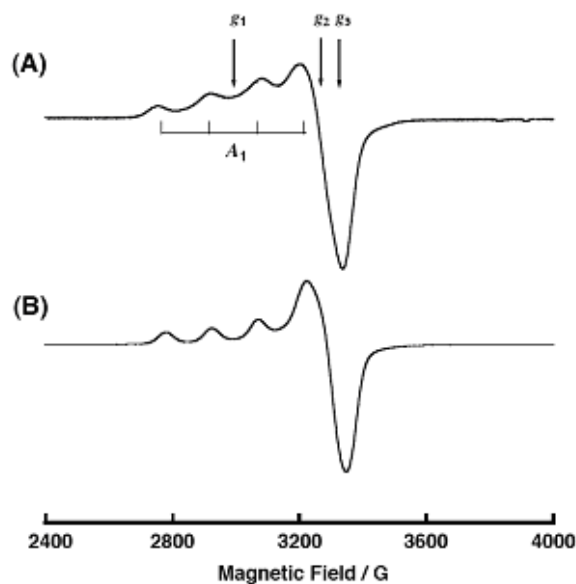


Figure 3.141: EPR spectrum of **1** in CH_3CN at -150°C showing g values of $g_1 = 2.250$, $g_2 = 2.065$, $g_3 = 2.030$, and hyperfine coupling constant $A_1 = 160$ G, $A_2 = 7$ G, and $A_3 = 5$ G. A. Kunishita, H. Ishimaru, S. Nakashima, T. Ogura, and S. Itoh, *J. Am. Chem. Soc.*, 2008, **130**, 4244. Copyright American Chemical Society (2008).

To determine the intermediate, a common radical trap 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was added. A 1:1 complex of intermediate and DMPO was isolated, and given the possible structure **2** (Figure 3.142), which is shown along with its EPR spectrum (Figure 3.143).

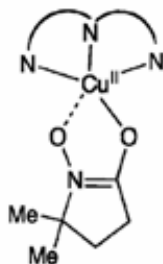


Figure 3.142: Proposed structure **2**, $\text{S} = \text{CH}_3\text{CN}$.

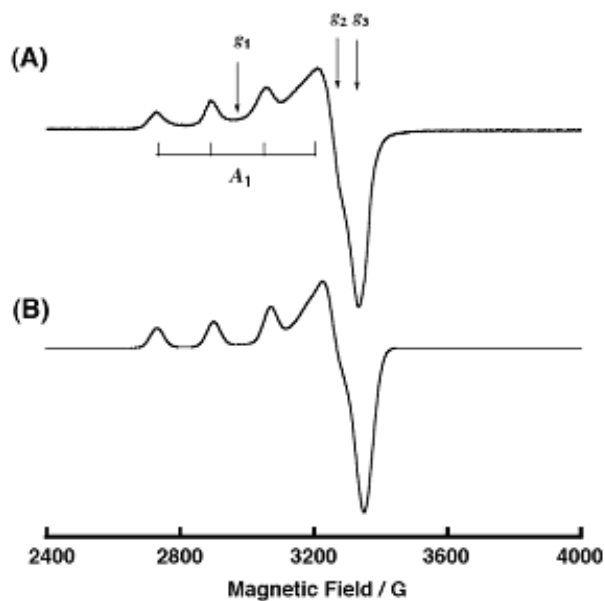


Figure 3.143: EPR spectrum of **1** in CH₃CN at -150 °C showing g values of $g_1 = 2.250$, $g_2 = 2.065$, $g_3 = 2.045$, and hyperfine coupling constant $A_1 = 170$ G, $A_2 = 25$ G, and $A_3 = 30$ G. A. Kunishita, H. Ishimaru, S. Nakashima, T. Ogura, and S. Itoh, *J. Am. Chem. Soc.*, 2008, **130**, 4244. Copyright American Chemical Society (2008).

The EPR data show similar though different spectra for Cu(II) in each compound, indicating a similar coordination environment – elongated axial, and most likely a LCu(II)O• intermediate.

3.8.2.1.2 Determination of a catalytic cycle

The mechanism of oxidizing alcohols to aldehydes using a Cu(II) catalyst, TEMPO, and O₂ was investigated using EPR. A proposed mechanism is given in Figure 3.144.

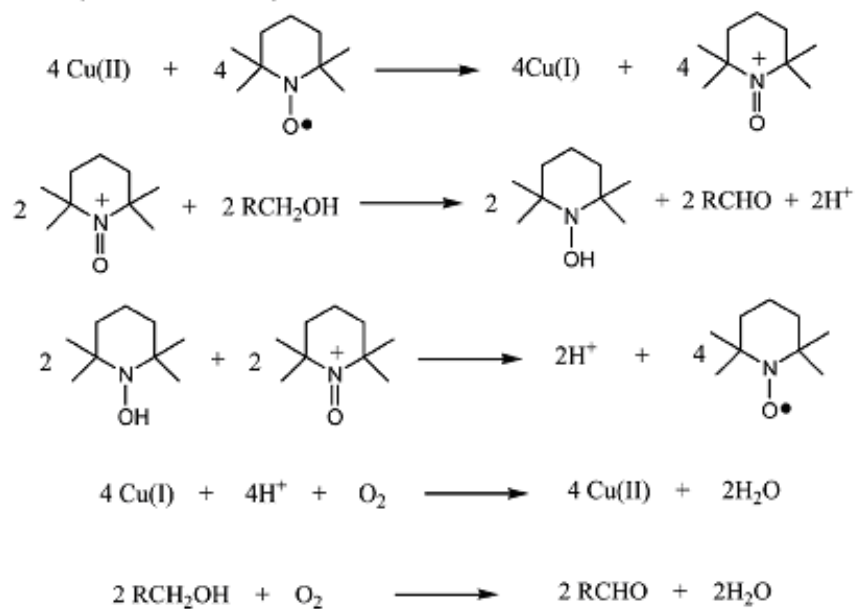


Figure 3.144: Proposed mechanism for the Cu(II) mediated oxidation of alcohols to aldehydes with TEMPO and O₂. M. Contel, P. R. Villuendas, J. Fernández-Gallardo, P. Alonso, J. M. Vincent, and R. Fish, *Inorg. Chem.*, 2005, **44**, 9771. Copyright American Chemical Society (2005).

EPR studies were conducted during the reaction by taking aliquots at various time points and immediately freezing the samples for EPR analysis. The resulting spectra are shown in Figure 3.145.

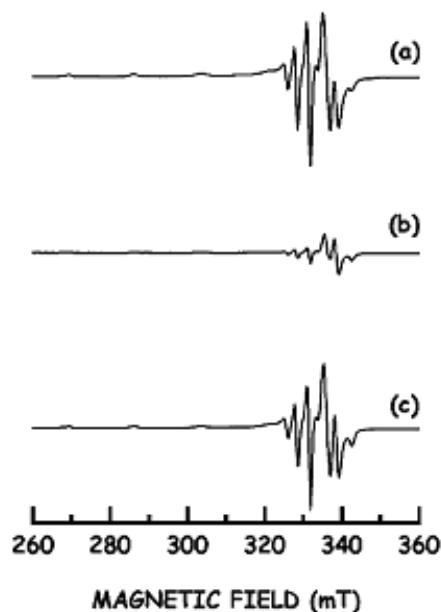


Figure 3.145: EPR spectra of reaction at (a) 1.2 h (b) 4 h (c) 8 h, M. Contel, P. R. Villuendas, J. Fernández-Gallardo, P. Alonso, J. M. Vincent, and R. Fish, *Inorg. Chem.*, 2005, **44**, 9771. Copyright American Chemical Society (2005).

The EPR spectrum (a) in Figure 6, after 1.2 hours shows a signal for TEMPO at $g = 2.006$ as well as a signal for Cu(II) with $g_{[U+2016]} = 2.26$, $g_{\perp} = 2.06$, $A_{[U+2016]} = 520$ MHz, and $A_{\perp} < 50$ MHz. After 4 hours, the signal for Cu(II) is no longer in the reaction mixture, and the TEMPO signal has decreased significantly. Suggesting that all the Cu(II) has been reduced to Cu(I) and the majority of TEMPO has been oxidized. After 8 hours, the signals for both Cu(II) and TEMPO have returned indicating regeneration of both species. In this way, EPR evidence supports the proposed mechanism.

3.8.2.1.3 Bibliography

- M. Contel, P. R. Villuendas, J. Fernández-Gallardo, P. Alonso, J. M. Vincent, and R. Fish, *Inorg. Chem.*, 2005, **44**, 9771.
- A. Kunishita, H. Ishimaru, S. Nakashima, T. Ogura, S. Itoh, *J. Am. Chem. Soc.*, 2008, **130**, 4244.
- G. Palmer, In *Physical Methods in Bioinorganic Chemistry Spectroscopy and Magnetism*. Ed. L. Que, University Science Books: Sausalito, CA (2000).
- J. Pilbrow, *Transition Ion Electron Paramagnetic Resonance*, Clarendon Press, Oxford (1990).
- J. Weil, J. Bolton, and J. Wertz, *Electron Paramagnetic Resonance: Elemental Theory and Practical Applications* John Wiley and Sons: New York (1994).

3.9 X-ray Photoelectron Spectroscopy

3.9.1 XPS of Carbon Nanomaterials²⁸

3.9.1.1 Introduction

X-ray photoelectron spectroscopy (XPS), also called electron spectroscopy for chemical analysis (ESCA), is a method used to determine the elemental composition of a material's surface. It can be further applied to determine the chemical or electronic state of these elements.

The photoelectric effect is the ejection of electrons from the surface of a material upon exposure to electromagnetic radiation of sufficient energy. Electrons emitted have characteristic kinetic energies proportional to the energy of the radiation, according to (3.19), where KE is the kinetic energy of the electron, h is Planck's constant, ν is the frequency of the incident radiation, E_b is the ionization, or binding, energy, and ϕ is the work function. The work function is a constant which is dependent upon the spectrometer.

$$\text{KE} = h\nu - E_b - \phi \quad (3.19)$$

In photoelectron spectroscopy, high energy radiation is used to expel core electrons from a sample. The kinetic energies of the resulting core electrons are measured. Using the equation with the kinetic energy and known frequency of radiation, the binding energy of the ejected electron may be determined. By Koopman's theorem, which states that ionization energy is equivalent to the negative of the orbital energy, the energy of the orbital from which the electron originated is determined. These orbital energies are characteristic of the element and its state.

3.9.1.2 Basics of XPS

3.9.1.2.1 Sample preparation

As a surface technique, samples are particularly susceptible to contamination. Furthermore, XPS samples must be prepared carefully, as any loose or volatile material could contaminate the instrument because of the ultra-high vacuum conditions. A common method of XPS sample preparation is embedding the solid sample into a graphite tape. Samples are usually placed on 1 x 1 cm or 3 x 3 cm sheets.

3.9.1.2.2 Experimental set-up

Monochromatic aluminum ($h\nu = 1486.6$ eV) or magnesium ($h\nu = 1253.6$ eV) K_α X-rays are used to eject core electrons from the sample. The photoelectrons ejected from the material are detected and their energies measured. Ultra-high vacuum conditions are used in order to minimize gas collisions interfering with the electrons before they reach the detector.

3.9.1.2.3 Measurement specifications

XPS analyzes material between depths of 1 and 10 nm, which is equivalent to several atomic layers, and across a width of about 10 μm . Since XPS is a surface technique, the orientation of the material affects the spectrum collected.

3.9.1.2.4 Data collection

X-ray photoelectron (XP) spectra provide the relative frequencies of binding energies of electrons detected, measured in electron-volts (eV). Detectors have accuracies on the order of ± 0.1 eV. The binding energies are used to identify the elements to which the peaks correspond. XPS data is given in a plot of intensity versus binding energy. Intensity may be measured in counts per unit time (such as counts per second, denoted c/s). Often, intensity is reported as arbitrary units (arb. units), since only relative intensities provide relevant

²⁸This content is available online at <<http://cnx.org/content/m34549/1.2/>>.

information. Comparing the areas under the peaks gives relative percentages of the elements detected in the sample. Initially, a survey XP spectrum is obtained, which shows all of the detectable elements present in the sample. Elements with low detection or with abundances near the detection limit of the spectrometer may be missed with the survey scan. Figure 3.146 shows a sample survey XP scan of fluorinated double-walled carbon nanotubes (DWNTs).

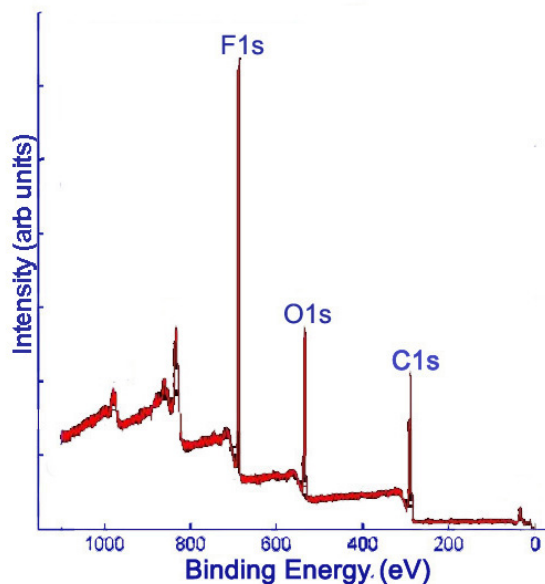


Figure 3.146: Survey XP spectrum of F-DWNTs (O. Kuznetsov, Rice University).

Subsequently, high resolution scans of the peaks can be obtained to give more information. Elements of the same kind in different states and environments have slightly different characteristic binding energies. Computer software is used to fit peaks within the elemental peak which represent different states of the same element, commonly called deconvolution of the elemental peak. Figure 3.147 and Figure 3.148 show high resolutions scans of C1s and F1s peaks, respectively, from Figure 3.146, along with the peak designations.

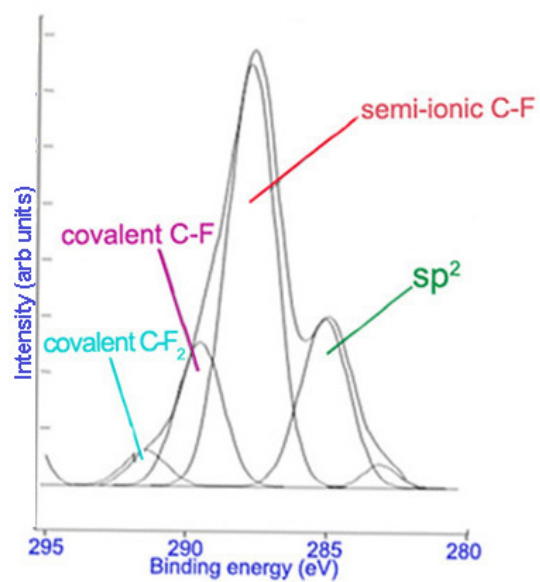


Figure 3.147: Deconvoluted high resolution C1s spectrum of F-DWNTs (O. Kuznetsov, Rice University).

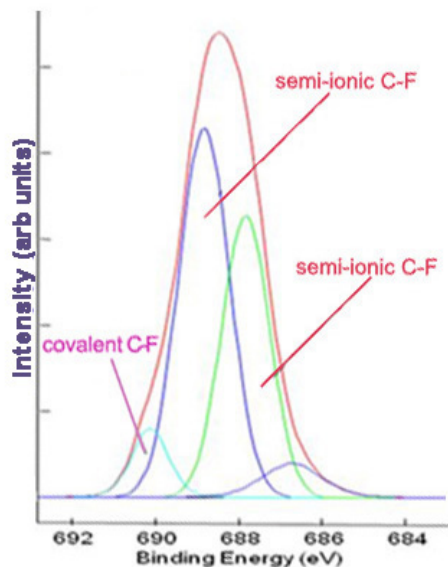


Figure 3.148: Deconvoluted high resolution F1s spectrum of F-DWNTs (O. Kuznetsov, Rice University).

3.9.1.2.5 Limitations

Both hydrogen and helium cannot be detected using XPS. For this reason, XPS can provide only relative, rather than absolute, ratios of elements in a sample. Also, elements with relatively low atomic percentages close to that of the detection limit or low detection by XPS may not be seen in the spectrum. Furthermore, each peak represents a distribution of observed binding energies of ejected electrons based on the depth of the atom from which they originate, as well as the state of the atom. Electrons from atoms deeper in the sample must travel through the above layers before being liberated and detected, which reduces their kinetic energies and thus increases their apparent binding energies. The width of the peaks in the spectrum consequently depends on the thickness of the sample and the depth to which the XPS can detect; therefore, the values obtained vary slightly depending on the depth of the atom. Additionally, the depth to which XPS can analyze depends on the element being detected.

High resolution scans of a peak can be used to distinguish among species of the same element. However, the identification of different species is discretionary. Computer programs are used to deconvolute the elemental peak. The peaks may then be assigned to particular species, but the peaks may not correspond with species in the sample. As such, the data obtained must be used cautiously, and care should be taken to avoid over-analyzing data.

3.9.1.3 XPS for carbon nanomaterials

Despite the aforementioned limitations, XPS is a powerful surface technique that can be used to accurately detect the presence and relative quantities of elements in a sample. Further analysis can provide information about the state and environment of atoms in the sample, which can be used to infer information about the surface structure of the material. This is particularly useful for carbon nanomaterials, in which surface

structure and composition greatly influence the properties of the material. There is much research interest in modifying carbon nanomaterials to modulate their properties for use in many different applications.

3.9.1.3.1 Sample preparation

Carbon nanomaterials present certain issues in regard to sample preparation. The use of graphite tape is a poor option for carbon nanomaterials because the spectra will show peaks from the graphite tape, adding to the carbon peak and potentially skewing or overwhelming the data. Instead, a thin indium foil (between 0.1 and 0.5 mm thick) is used as the sample substrate. The sample is simply pressed onto a piece of the foil.

3.9.1.4 Analysis and applications for carbon nanomaterials

3.9.1.4.1 Chemical Speciation

The XP survey scan is an effective way to determine the identity of elements present on the surface of a material, as well as the approximate relative ratios of the elements detected. This has important implications for carbon nanomaterials, in which surface composition is of greatest importance in their uses. XPS may be used to determine the purity of a material. For example, nanodiamond powder is created by detonation, which can leave nitrogenous groups and various oxygen containing groups attached to the surface. Figure 3.149 shows a survey scan of a nanodiamond thin film with the relative atomic percentages of carbon, oxygen, and nitrogen being 91.25%, 6.25%, and 1.7%, respectively. Based on the XPS data, the nanodiamond material is approximately 91.25% pure.

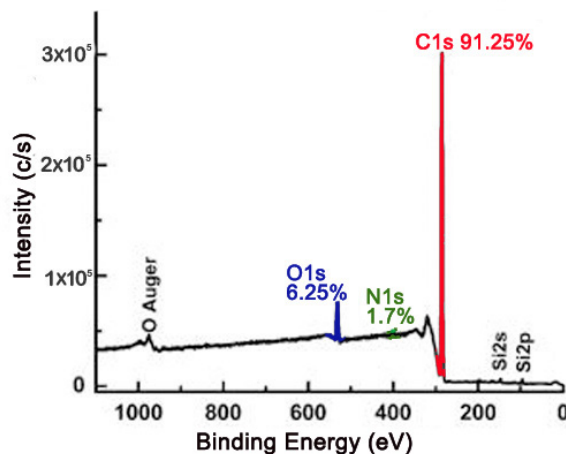


Figure 3.149: Survey XPS of a nanodiamond thin film. Adapted from F. Y. Xie, W. G. Xie, J. Chen, X. Liu, D. Y. Lu, and W. H. Zhang, *J. Vac. Sci. Tech. B*, 2008, **26**, 102.

XPS is a useful method to verify the efficacy of a purification process. For example, high-pressure CO conversion single-walled nanotubes (HiPco SWNTs) are made using iron as a catalyst. Figure 3.150 shows the Fe2p XP spectra for pristine and purified HiPco SWNTs.

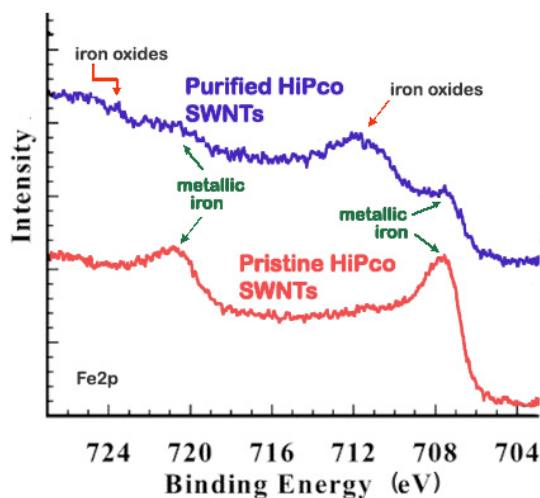


Figure 3.150: High resolution scan of Fe2p peak for pristine and purified HiPco SWNTs. Adapted with permission from C. M. Yang, H. Kanoh, K. Kaneko, M. Yudasaka, and S. Iijima, *J. Phys. Chem. B*, 2002, **106**, 8994. Copyright: American Chemical Society (2002).

For this application, XPS is often done in conjunction with thermogravimetric analysis (TGA), which measures the weight lost from a sample at increasing temperatures. TGA data serves to corroborate the changes observed with the XPS data by comparing the percentage of weight loss around the region of the impurity suspected based on the XP spectra. The TGA data support the reduction in iron content with purification suggested by the XP spectra above, for the weight loss at temperatures consistent with iron loss decreases from 27% in pristine SWNTs to 18% in purified SWNTs. Additionally, XPS can provide information about the nature of the impurity. In Figure 3.150, the Fe2p spectrum for pristine HiPco SWNTs shows two peaks characteristic of metallic iron at 707 and 720 eV. In contrast, the Fe2p spectrum for purified HiPco SWNTs also shows two peaks at 711 and 724 eV, which are characteristic of either Fe_2O_3 or Fe_3O_4 . In general, the atomic percentage of carbon obtained from the XPS spectrum is a measure of the purity of the carbon nanomaterials.

3.9.1.4.2 Bonding and functional groups

XP spectra give evidence of functionalization and can provide insight into the identity of the functional groups. Carbon nanomaterials provide a versatile surface which can be functionalized to modulate their properties. For example, the sodium salt of phenyl sulfonated SWNTs is water soluble. In the XP survey scan of the phenyl sulfonated SWNTs, there is evidence of functionalization owing to the appearance of the S2p peak. Figure 3.151 shows the survey XP spectrum of phenyl sulfonated SWNTs.

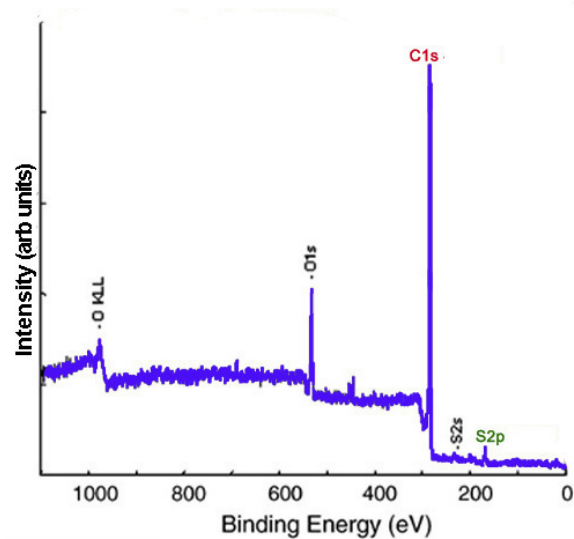


Figure 3.151: Survey XP spectrum of phenyl sulfonated SWNTs. Adapted with permission from F. Liang, J. M. Beach, P. K. Rai, W. H. Guo, R. H. Hauge, M. Pasquali, R. E. Smalley, and W. E. Billups, *Chem. Mater.*, 2006, **18**, 1520. Copyright: American Chemical Society (2006).

The survey XP spectrum of the sodium salt shows a Na1s peak (Figure 3.152) and the high resolution scans of Na1s and S2p show that the relative atomic percentages of Na1s and S2p are nearly equal (Figure 3.153), which supports the formation of the sodium salt.

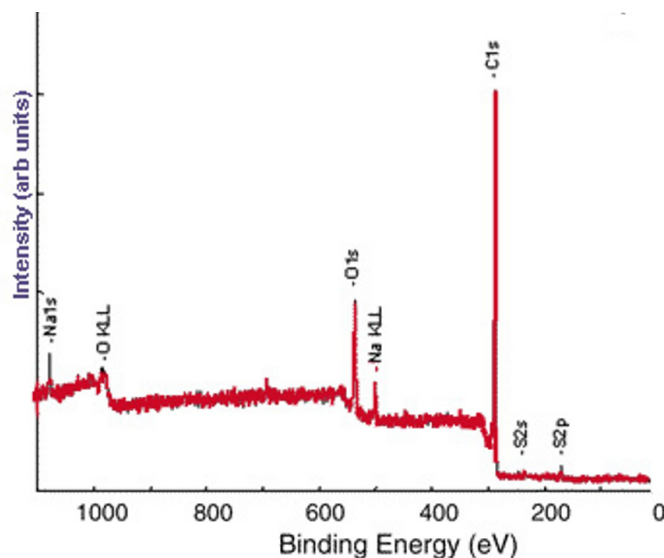


Figure 3.152: Survey XP spectrum of phenyl sulfonated SWNTs. Adapted with permission from F. Liang, J. M. Beach, P. K. Rai, W. H. Guo, R. H. Hauge, M. Pasquali, R. E. Smalley, and W. E. Billups, *Chem. Mater.*, 2006, **18**, 1520. Copyright: American Chemical Society (2006).

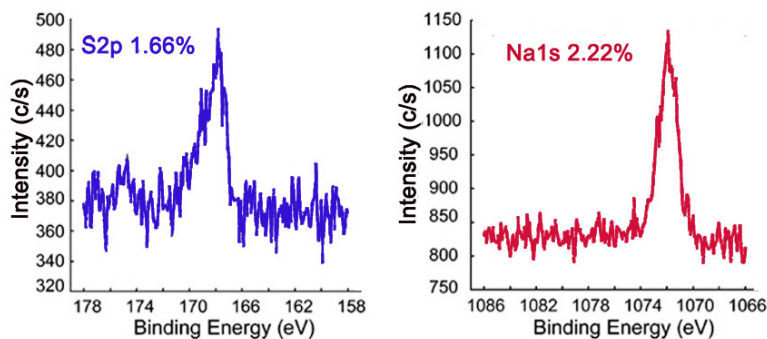


Figure 3.153: High resolution S2p (left) and Na1s (right) XP spectra of phenyl sulfonated SWNTs. Adapted with permission from F. Liang, J. M. Beach, P. K. Rai, W. H. Guo, R. H. Hauge, M. Pasquali, R. E. Smalley, and W. E. Billups, *Chem. Mater.*, 2006, **18**, 1520. Copyright: American Chemical Society (2006).

3.9.1.4.3 Further characterization

High resolution scans of each of the element peaks of interest can be obtained to give more information about the material. This is a way to determine with high accuracy the presence of elements as well as relative ratios of elements present in the sample. This can be used to distinguish species of the same element in different chemical states and environments, such as through bonding and hybridization, present in the material. The distinct peaks may have binding energies that differ slightly from that of the convoluted elemental peak. Assignment of peaks can be done using XPS databases, such as that produced by NIST²⁹. The ratios of the intensities of these peaks can be used to determine the percentage of atoms in a particular state. Discrimination between and identity of elements in different states and environments is a strength of XPS that is of particular interest for carbon nanomaterials.

3.9.1.4.3.1 Hybridization

The hybridization of carbons influences the properties of a carbon nanomaterial and has implications in its structure. XPS can be used to determine the hybridization of carbons on the surface of a material, such as graphite and nanodiamond. Graphite is a carbon material consisting of sp^2 carbons. Thus, theoretically the XPS of pure graphite would show a single C1s peak, with a binding energy characteristic of sp^2 carbon (around 284.2 eV). On the other hand, nanodiamond consists of sp^3 bonded carbons. The XPS of nanodiamond should show a single C1s peak, with a binding energy characteristic of sp^3 carbon (around 286 eV). The ratio of the sp^2 and sp^3 peaks in the C1s spectrum gives the ratio of sp^2 and sp^3 carbons in the nanomaterial. This ratio can be altered and compared by collecting the C1s spectra. For example, laser treatment of graphite creates diamond-like material, with more sp^3 character when a higher laser power is used. This can be observed in Figure 3.154, in which the C1s peak is broadened and shifted to higher binding energies as increased laser power is applied.

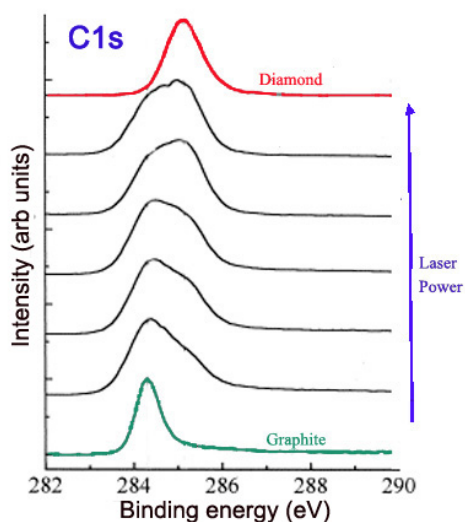


Figure 3.154: C1s high resolution XP spectra of graphite, nanodiamond, and graphite samples with increasing laser power treatment. Adapted from P. Merel, M. Tabbal, M. Chaker, S. Moisa, and J. Margot, *Appl. Surf. Sci.*, 1998, **136**, 105.

²⁹<http://srdata.nist.gov/xps/Default.aspx>

Alternatively, annealing nanodiamond thin films at very high temperatures creates graphitic layers on the nanodiamond surface, increasing sp^2 content. The extent of graphitization increases with the temperature at which the sample is annealed, as shown in Figure 3.155.

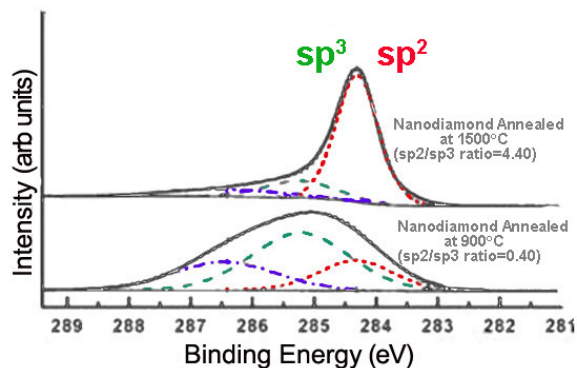


Figure 3.155: Deconvoluted high resolution C1s XP spectra for annealed nanodiamond. Adapted from F. Y. Xie, W. G. Xie, J. Chen, X. Liu, D. Y. Lu, and W. H. Zhang, *J. Vac. Sci. Tech. B*, 2008, **26**, 102.

3.9.1.4.3.2 Reaction completion

Comparing the relative intensities of various C1s peaks can be powerful in verifying that a reaction has occurred. Fluorinated carbon materials are often used as precursors to a broad range of variously functionalized materials. Reaction of fluorinated SWNTs (F-SWNTs) with polyethyleneimine (PEI) leads to decreases in the covalent carbon-fluoride C1s peak, as well as the evolution of the amine C1s peak. These changes are observed in the C1s spectra of the two samples (Figure 3.156).

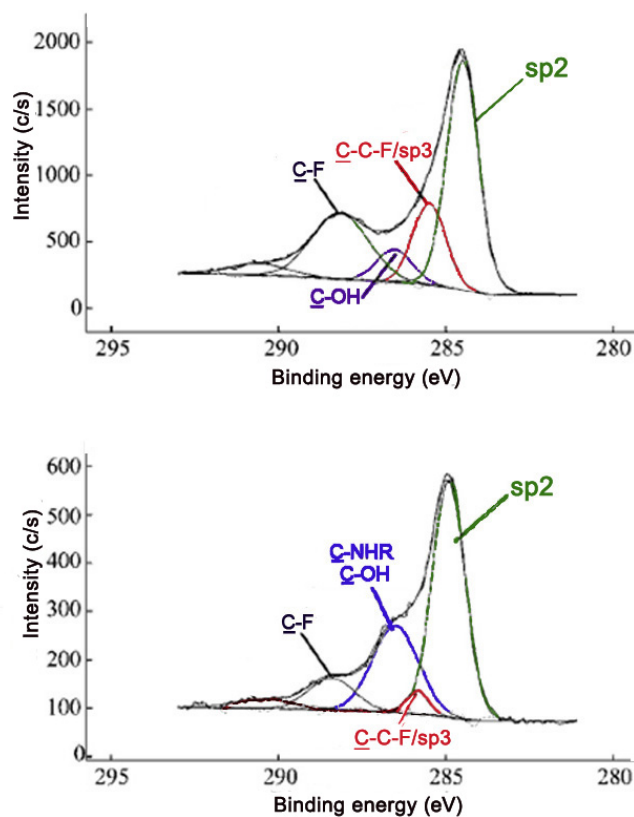


Figure 3.156: High resolution C1s XP spectra of F-SWNTs (top) and PEI-SWNTs (bottom). Adapted with permission from E. P. Dillon, C. A. Crouse, and A. R. Barron, *ACS Nano*, 2008, **2**, 156. Copyright: American Chemical Society (2008).

3.9.1.4.3.3 Nature and extent of functionalization

XPS can also be applied to determine the nature and extent of functionalization. In general, binding energy increases with decreasing electron density about the atom. Species with more positive oxidation states have higher binding energies, while more reduced species experience a greater degree of shielding, thus increasing the ease of electron removal.

The method of fluorination of carbon materials and such factors as temperature and length of fluorination affect the extent of fluoride addition as well as the types of carbon-fluorine bonds present. A survey scan can be used to determine the amount of fluorine compared to carbon. High resolution scans of the C1s and F1s peaks can also give information about the proportion and types of bonds. A shift in the peaks, as well as changes in peak width and intensity, can be observed in spectra as an indication of fluorination of graphite. Figure 3.157 shows the C1s and F1s spectra of samples containing varying ratios of carbon to fluorine.

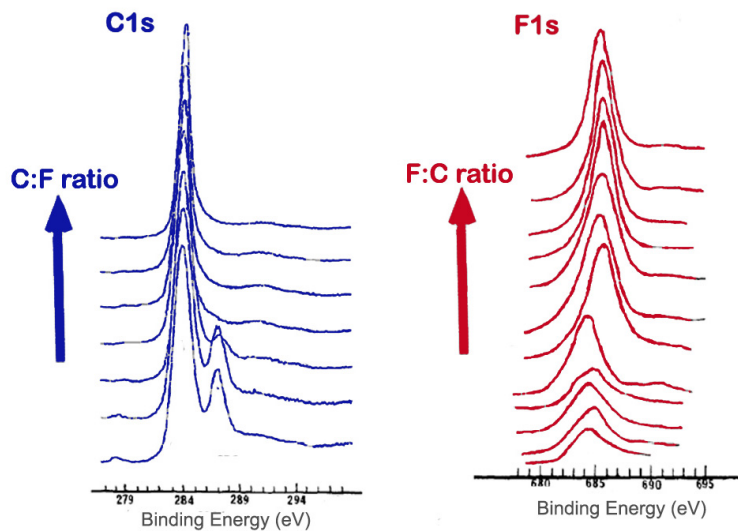


Figure 3.157: C1s and F1s high resolution XP spectra for graphite fluorides. Adapted from I. Palchan, M. Crespin, H. Estrade-Szwarczkopf, and B. Rousseau. *Chem. Phys. Lett.*, 1989, **157**, 321.

Furthermore, different carbon-fluorine bonds show characteristic peaks in high resolution C1s and F1s spectra. The carbon-fluorine interactions in a material can range from ionic to covalent. Covalent carbon-fluorine bonds show higher core electron binding energies than bonds more ionic in character. The method of fluorination affects the nature of the fluorine bonds. Graphite intercalation compounds are characterized by ionic carbon-fluorine bonding. Figure 3.158 shows the F1s spectra for two fluorinated exfoliated graphite samples prepared with different methods.

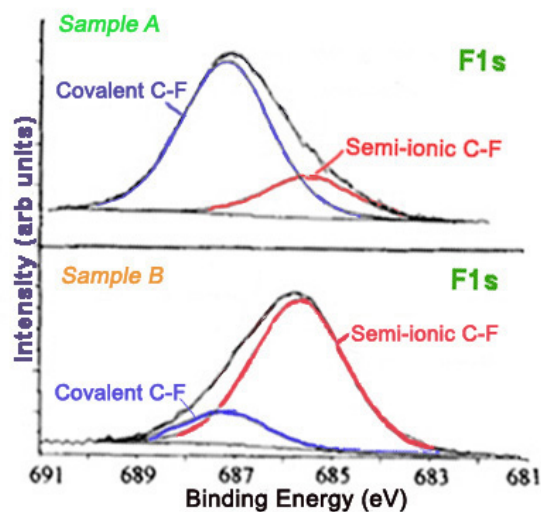


Figure 3.158: High resolution F1s XP spectra of two fluorinated exfoliated graphite samples. Adapted from A. Tressaud, F. Moguet, S. Flandrois, M. Chambon, C. Guimon, G. Nanse, E. Papirer, V. Gupta, and O.P. Bahl. *J. Phys. Chem. Solids*, 1996, **57**, 745.

Also, the peaks for carbons attached to a single fluorine atom, two fluorine atoms, and carbons attached to fluorines have characteristic binding energies. These peaks are seen in that C1s spectra of F- and PEI-SWNTs shown in Figure 3.159.

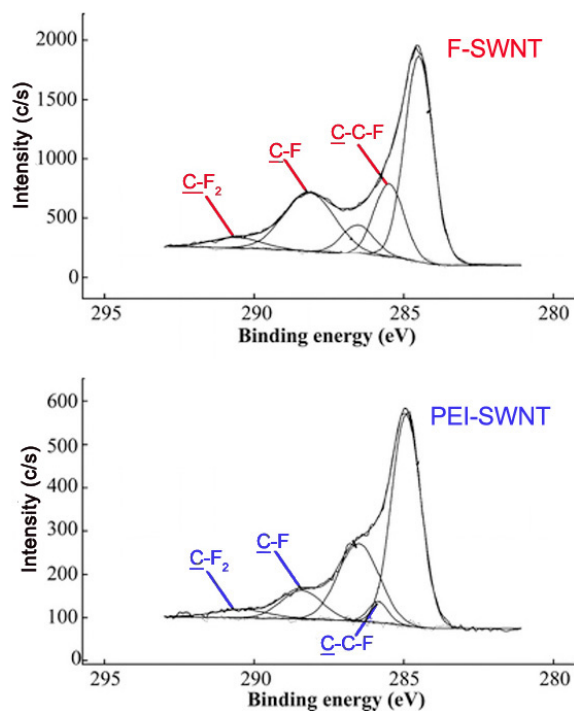


Figure 3.159: High resolution C1s XP spectra of F-SWNTs (top) and PEI-SWNTs (bottom). Adapted with permission from E. P. Dillon, C. A. Crouse, and A. R. Barron, *ACS Nano*, 2008, **2**, 156. Copyright: American Chemical Society (2008).

Table 3.20 lists various bonds and functionalities and the corresponding C1s binding energies, which may be useful in assigning peaks in a C1s spectrum, and consequently in characterizing the surface of a material.

Bond/Group	Binding Energy (eV)
C-C	284.0-286.0
C-C (sp^2)	284.3-284.6
C-C (sp^3)	285.0-286.0
C-N	285.2-288.4
C-NR ₂ (amine)	285.5-286.4
O=C-NH (amide)	287.9-288.6
-C $\equiv$ N (nitrile)	266.3-266.8
C-O	286.1-290.0
O=C-OH (carboxyl)	288.0-289.4
-C-O (epoxy)	286.1-287.1
-C-OH (hydroxyl)	286.4-286.7
-C-O-C- (ether)	286.1-288.0
-C=O (aldehyde/ketone)	287.1-288.1
C-F	287.0-293.4
-C-F (covalent)	287.7-290.2
-C-F (ionic)	287.0-287.4
$\underline{\text{C}}$ -C-F	286.0-287.7
C-F ₂	291.6-292.4
C-F ₃	292.4-293.4
C-S	285.2-287.5
C-Cl	287.0-287.2

Table 3.20: Summary of selected C1s binding energies.

3.9.1.4.4 Conclusion

X-ray photoelectron spectroscopy is a facile and effective method for determining the elemental composition of a material's surface. As a quantitative method, it gives the relative ratios of detectable elements on the surface of the material. Additional analysis can be done to further elucidate the surface structure. Hybridization, bonding, functionalities, and reaction progress are among the characteristics that can be inferred using XPS. The application of XPS to carbon nanomaterials provides much information about the material, particularly the first few atomic layers, which are most important for the properties and uses of carbon nanomaterials.

3.9.1.5 Bibliography

- J. Bockris, *Modern Electrochemistry 2A*, 2nd ed., Springer (2001).
- E. P. Dillon, C. A. Crouse, and A. R. Barron, *ACS Nano*, 2008, **2**, 156.
- Y. G. Gogotsi, and I. V. Uvarova, *Nanostructured materials and coatings for biomedical and sensor applications*, Kluwer Academic Publishing (2003).
- F. Liang, J. M. Beach, P. K. Rai, W. H. Guo, R. H. Hauge, M. Pasquali, R. E. Smalley, and W. E. Billups, *Chem. Mater.*, 2006, **18**, 1520.

- P. Merel, M. Tabbal, M. Chaker, S. Moisa, and J. Margot, *Appl. Surf. Sci.*, 1998, **136**, 105.
- T. Nakajima, *Graphite fluorides and carbon-fluorine compounds*, CRC Press, Boca Raton (1991).
- I. Palhan, M. Crespín, H. Estrade-Szwarckopf, and B. Rousseau. *Chem. Phys. Lett.*, 1989, **157**, 321.
- A. Tressaud, F. Moguet, S. Flandrois, M. Chambon, C. Guimon, G. Nanse, E. Papirer, V. Gupta, and O. P. Bahl. *J. Phys. Chem. Solids*, 1996, **57**, 745.
- F. Y. Xie, W. G. Xie, J. Chen, X. Liu, D. Y. Lu, and W. H. Zhang, *J. Vac. Sci. Tech. B*, 2008, **26**, 102.
- C. M. Yang, H. Kanoh, K. Kaneko, M. Yudasaka, and S. Iijima, *J. Phys. Chem. B*, 2002, **106**, 8994.

3.10 ESI-QTOF-MS Coupled to HPLC and its Application for Food Safety³⁰

3.10.1 Introduction

High-performance liquid chromatography (HPLC) is a very powerful separation method widely used in environmental science, pharmaceutical industry, biological and chemical research and other fields. Generally, it can be used to purify, identify and/or quantify one or several components in a mixture simultaneously.

Mass spectrometry (MS) is a detection technique by measuring mass-to-charge ratio of ionic species. The procedure consists of different steps. First, a sample is injected in the instrument and then evaporated. Second, species in the sample are charged by certain ionized methods, such as electron ionization (EI), electrospray ionization (ESI), chemical ionization (CI), matrix-assisted laser desorption/ionization (MALDI). Finally, the ionic species will be analyzed depending on their mass-to-charge ratio (m/z) in the analyzer, such as quadrupole, time-of-flight (TOF), ion trap and fourier transform ion cyclotron resonance.

The mass spectrometric identification is widely used together with chromatographic separation. The most common ones are gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-mass spectrometry (LC-MS). Because of the high sensitivity, selectivity and relatively low price of GC-MS, it has very wide applications in drug detection, environmental analysis and so forth. For those organic chemistry research groups, it is also a daily-used and convenient equipment. However, GC-MS is ineffective if the molecules have high boiling point and/or will be decomposed at high temperature.

In this module, we will mainly talk about liquid chromatography and electrospray ionization quadrupole time-of-flight mass spectrometry (LC/ESI-QTOF-MS). As mentioned above, the LC has an efficient capacity of separation and MS has a high sensitivity and strong ability of structural characterization. Furthermore, TOF-MS, has several distinctive properties on top of regular MS, including fast acquisition rates, high accuracy in mass measurements and a large mass range. The combination of LC and ESI-TOF-MS allow us to obtain a powerful in the quantitative and qualitative analysis of molecules in complex matrices by reducing the matrix interferences. It may play an important role in the area of food safety.

3.10.2 How it works

Generally, LC-MS has four components, including an autosampler, HPLC, ionization source and mass spectrometer, as shown in Figure 3.160. Here we need to pay attention to the interface of HPLC and MS so that they can be suitable to each other and be connected. There are specified separation column for HPLC-MS, whose inner diameter (I.D.) is usually 2.0 mm. And the flow rate, which is 0.05 - 0.2 mL/min, is slower than typical HPLC. For the mobile phase, we use the combination of water and methanol and/acetonitrile. And because ions will inhibit the signals in MS, if we want to modify to mobile phase, the modifier should be volatile, such as HCO_2H , $\text{CH}_3\text{CO}_2\text{H}$, $[\text{NH}_4][\text{HCO}_2]$ and $[\text{NH}_4][\text{CH}_3\text{CO}_2]$.

³⁰This content is available online at <<http://cnx.org/content/m38334/1.1/>>.

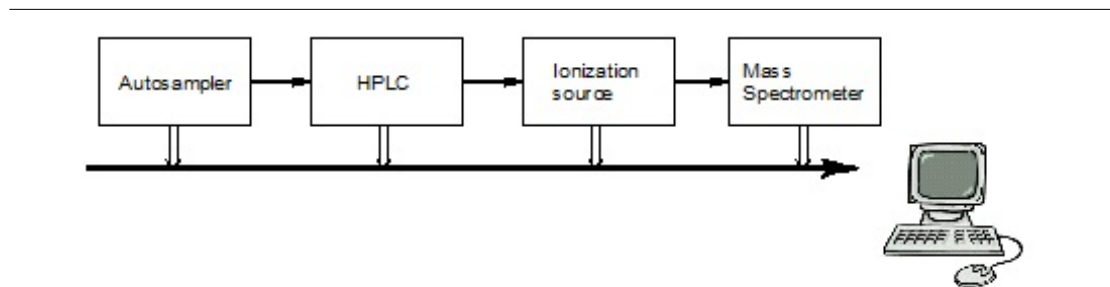


Figure 3.160: The component of a HPCL-MS system. Adapted from W. A . Korfmacher, *Drug Discov. Today*, 2005, **10**, 1357.

As the interface between HPLC and MS, the ionization source is also important. There are many types and ESI and atmospheric pressure chemical ionization (APCI) are the most common ones. Both of them are working at atmospheric pressure, high voltage and high temperature. In ESI, the column eluent is nebulized in high voltage field (3 - 5 kV). Then there will be very small charged droplet. Finally individual ions are formed in this process and go into the mass spectrometer.

3.10.3 Comparison of ESI-QTOF-MS and other mass spectrometer methods

There are many types of mass spectrometers which can connect with the HPLC. One of the most widely-used MS systems is the single quadrupole mass spectrometer, which is not very expensive, shown in Figure 3.161. This system has two modes. One mode is *total ion monitoring* (TIM) mode which can provide the total ion chromatograph. The other is *selected ion monitoring* (SIM) mode, in which the user can choose to monitor some specific ions, and the latter's sensitivity is much higher than the former's. Further, the mass resolution of the single quadrupole mass spectrometer is 1 Da and its largest detection mass range is 30 - 3000 Da.

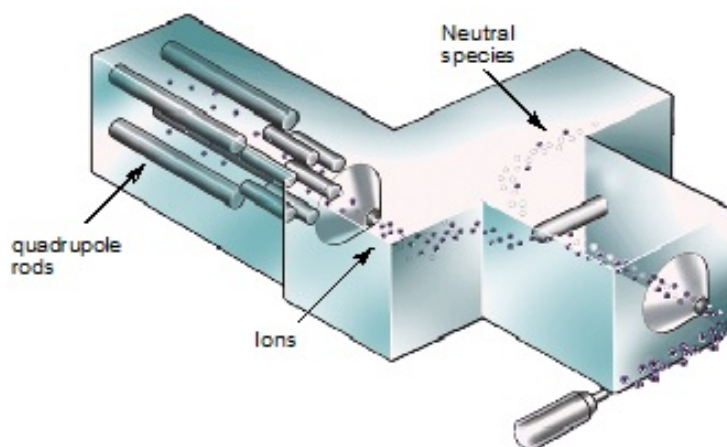


Figure 3.161: Single quadrupole mass spectrometer. Adapted from W. A. Korfmacher, *Using Mass Spectrometry for Drug Metabolism Studies*, 1st Edition, Taylor & Francis, Abingdon (2004).

The second MS system is the triple quadrupole MS-MS system, shown in Figure 3.162. Using this system, people can select some ions, called parent ions, and use another electron beam to collide them again to get the fragment ions, called daughter ions. In other words, there are two steps to select the target molecules. So it reduces the matrix effect a lot. This system is very useful in the analysis of biological samples because biological samples always have a very complex matrix; however, the mass resolution is still 1 Da.

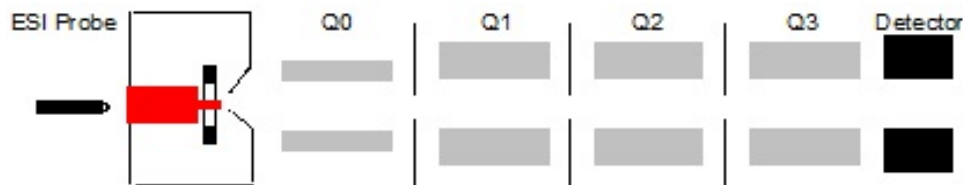


Figure 3.162: Triple quadrupole mass spectrometer. Adapted from W. A. Korfmacher, *Using Mass Spectrometry for Drug Metabolism Studies*, 1st Edition, Taylor & Francis, Abingdon (2004).

The third system is time-of-flight (TOF) MS, shown in Figure 3.163, which can provide a higher mass resolution spectrum, 3 to 4 decimals of Da. Furthermore, it can detect a very large range of mass at a very fast speed. The largest detection mass range is 20 - 10000 Da. But the price of this kind of MS is very high. The last technique is a hybrid mass spectrometer, Q-TOF MS, which combines a single quadrupole MS and a TOF MS. Using this MS, we can get high resolution chromatograph and we also can use the MS-MS system to identify the target molecules.

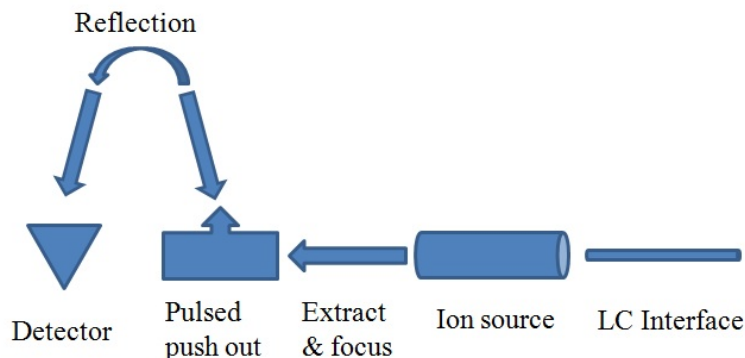


Figure 3.163: Time-of-flight mass spectrometer. Adapted from W. A. Korfmacher, *Using Mass Spectrometry for Drug Metabolism Studies*, 1st Edition, Taylor & Francis, 2004.

3.10.4 Application of LC/ESI-QTOF-MS in the detection of quinolones in edible animal food

Quinolones are a family of common antibacterial veterinary medicine which can inhibit DNA-gyrase in bacterial cells. However, the residues of quinolone in edible animal products may be directly toxic or cause resistant pathogens in humans. Therefore, sensitive methods are required to monitor such residues possibly present in different animal-producing food, such as eggs, chicken, milk and fish. The molecular structures of eight quinolones, ciprofloxacin (CIP), anofloxacin methanesulphonate (DAN), enrofloxacin (ENR), difloxacin (DIF), sarafloxacin (SARA), oxolinic acid (OXO), flumequine (FLU), ofloxacin (OFL), are shown in Figure 3.164.

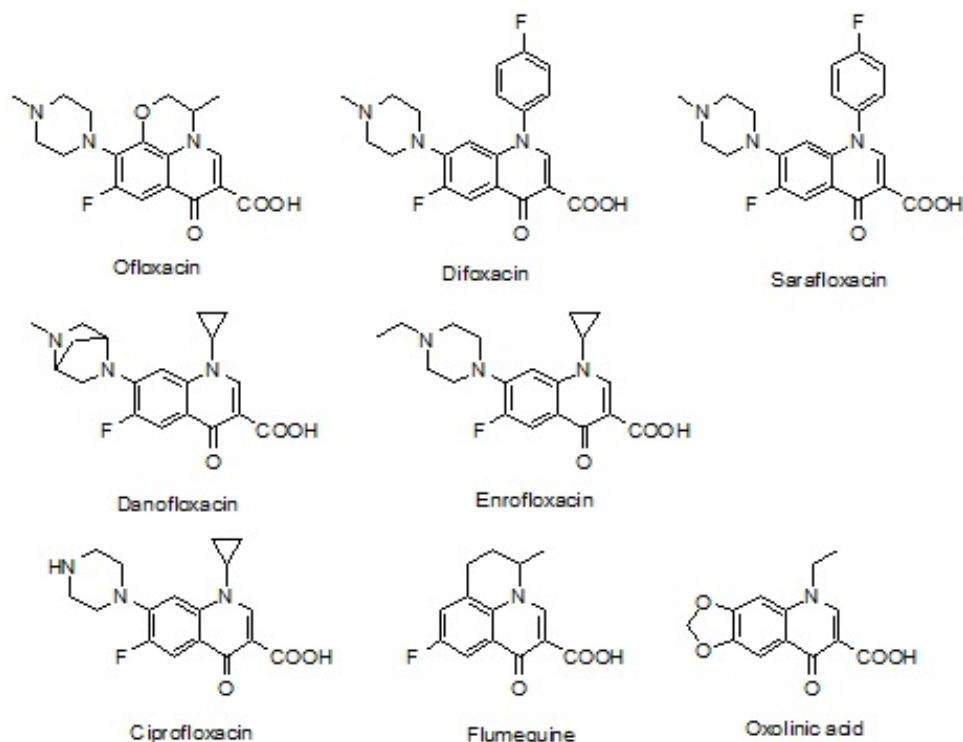


Figure 3.164: The molecular structure of eight quinolones. Adapted from M. M. Zheng, G. D. Ruan, and Y. Q. Feng, *J. Chromatogr. A*, 2009, **1216**, 7510.

LC-MS is a common detection approach in the field of food safety. But because of the complex matrix of the samples, it is always difficult to detect those target molecules of low concentration by using single quadrupole MS. The following gives an example of the application of LC/ESI-QTOF-MS.

Using a quaternary pump system, a Q-TOF-MS system, a C18 column (250 mm $\times$ 2.0 mm I.D., 5 μ m) with a flow rate of 0.2 mL/min, and a mixture of solvents as the mobile phase comprising of 0.3% formic acid solution and acetonitrile. The gradient profile for mobile phase is shown in Table 3.21. Since at acidic pH condition, the quinolones carried a positive charge, all mass spectra were acquired in the positive ion mode and summarizing 30,000 single spectra in the mass range of 100-500 Da.

Time (min)	Volume % of formic acid solution	Volume % of acetonitrile
0	80	20
12	65	35
15	20	80
20	15	85
30	15	85
30.01	80	20

Table 3.21: The gradient profile for mobile phase.

The optimal ionization source working parameters were as follows: capillary voltage 4.5 kV; ion energy of quadrupole 5 eV/z; dry temperature 200 °C; nebulizer 1.2 bar; dry gas 6.0 L/min. During the experiments, HCO₂Na (62 Da) was used to externally calibrate the instrument. Because of the high mass accuracy of the TOF mass spectrometer, it can extremely reduce the matrix effects. Three different chromatographs are shown in Figure 3.165. The top one is the total ion chromatograph at the window range of 400 Da. It's impossible to distinguish the target molecules in this chromatograph. The middle one is at one Da resolution, which is the resolution of single quadrupole mass spectrometer. In this chromatograph, some of the molecules can be identified. But noise intensity is still very high and there are several peaks of impurities with similar mass-to-charge ratios in the chromatograph. The bottom one is at 0.01 Da resolution. It clearly shows the peaks of eight quinolones with very high signal to noise ratio. In other words, due to the fast acquisition rates and high mass accuracy, LC/TOF-MS can significantly reduce the matrix effects.

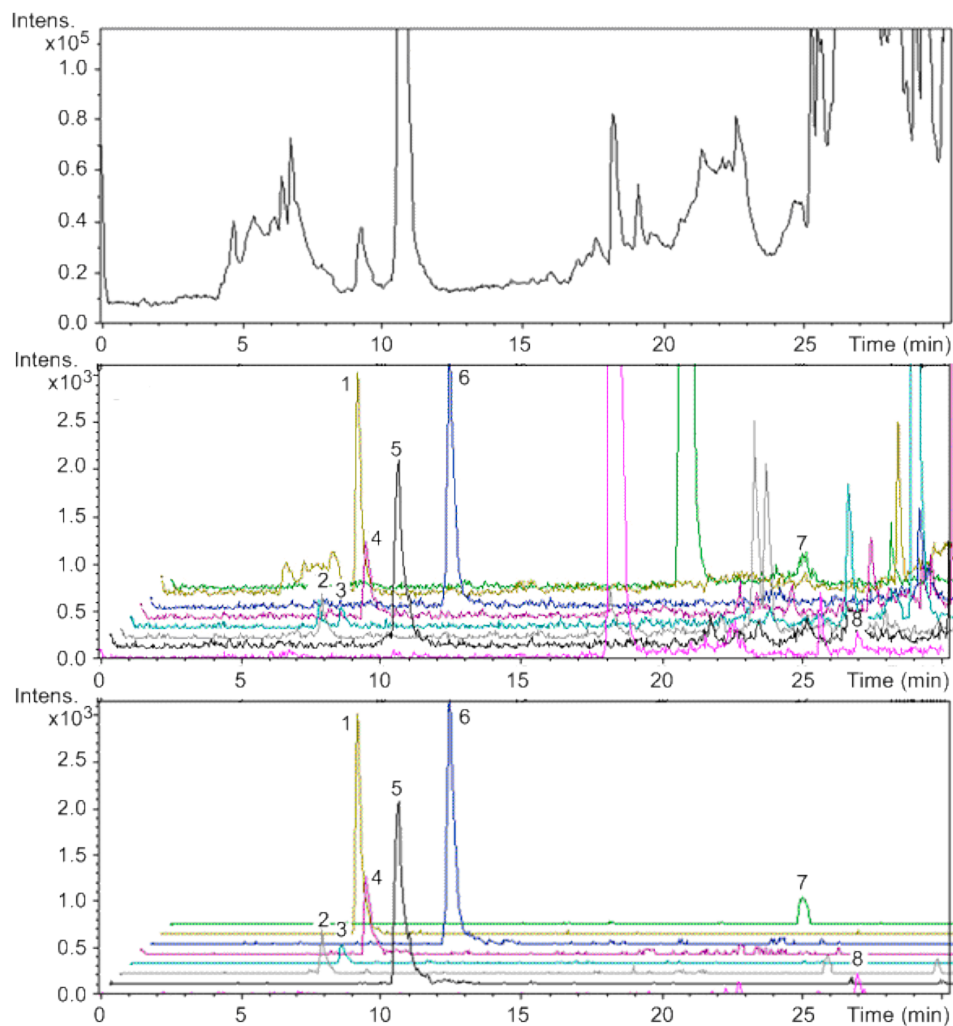


Figure 3.165: Different chromatographs of 4 ng/g eight quinolones spiked in fish samples at different mass resolutions. Peaks: 1 = OFL; 2 = CIP; 3 = DAN; 4 = ENR; 5 = SARA; 6 = DIF; 7 = OXO; 8 = FLU. Adapted from M. M. Zheng, G. D. Ruan, and Y. Q. Feng, *J. Chromatogr. A*, 2009, **1216**, 7510.

The quadrupole MS can be used to further confirm the target molecules. Figure 3.166 shows the chromatograms obtained in the confirmation of CIP (17.1 ng/g) in a positive milk sample and ENR (7.5 ng/g) in a positive fish sample. The chromatographs of parent ions are shown on the left side. On the right side, they are the characteristic daughter ion mass spectra of CIP and ENR.

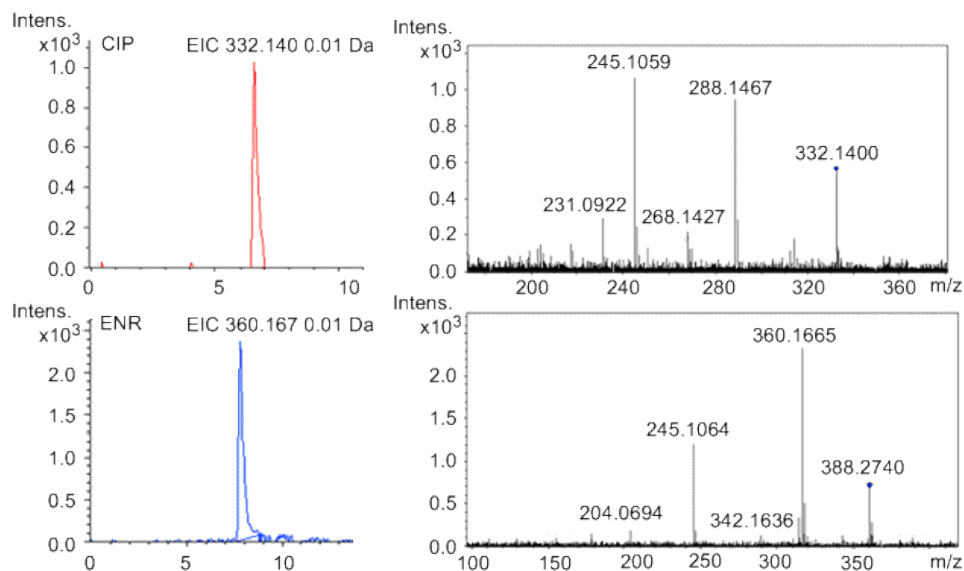


Figure 3.166: Chromatograms obtained in the confirmation of CIP (17.1 ng/g) in positive milk sample and ENR (7.5 ng/g) in positive fish sample. Adapted from M. M. Zheng, G. D. Ruan, and Y. Q. Feng, *J. Chromatogr. A*, 2009, **1216**, 7510.

3.10.5 Drawbacks of LC/Q-TOF-MS

Some of the drawbacks of LC/Q-TOF-MS are its high costs of purchase and maintenance. It is hard to apply this method in daily detection in the area of environmental protection and food safety.

In order to reduce the matrix effect and improve the detection sensitivity, people may use some sample preparation methods, such as liquid-liquid extraction (LLE), solid-phase extraction (SPE), distillation. But these methods would consume large amount of samples, organic solvent, time and efforts. Nowadays, there appear some new sample preparation methods. For example, people may use online microdialysis, supercritical fluid extraction (SFE) and pressurized liquid extraction. In the method mentioned in the Application part, we use online in-tube solid-phase microextraction (SPME), which is an excellent sample preparation technique with the features of small sample volume, simplicity solventless extraction and easy automation.

3.10.6 Bibliography

- M. S. Lee and E. H. Kerns, *Mass Spec. Rev.*, 1999, **18**, 187.
- W. A. Korfmacher, *Drug Discov. Today*, 2005, **10**, 1357.
- W. A. Korfmacher, *Using Mass Spectrometry for Drug Metabolism Studies*, 1st Edition, Taylor & Francis, Abingdon (2004).
- C. Zwiener and F. H. Frimmel, *Anal. Bioanal. Chem.*, 2004, **378**, 851.
- M. M. Zheng, G. D. Ruan, and Y. Q. Feng, *J. Chromatogr. A*, 2009, **1216**, 7510.

3.11 Mass Spectrometry

3.11.1 Principles of Mass Spectrometry and Modern Applications³¹

3.11.1.1 Introduction

Mass spectrometry (MS) is a powerful characterization technique used for the identification of a wide variety of chemical compounds. At its simplest, MS is merely a tool for determining the molecular weight of the chemical species in a sample. However, with the high resolution obtainable from modern machines, it is possible to distinguish isomers, isotopes, and even compounds with nominally identical molecular weights. Libraries of mass spectra have been compiled which allow rapid identification of most known compounds, including proteins as large as 100 kDa (100,000 amu).

Mass spectrometers separate compounds based on a property known as the mass-to-charge ratio. The sample to be identified is first ionized, and then passed through some form of magnetic field. Based on parameters such as how long it takes the molecule to travel a certain distance or the amount of deflection caused by the field, a mass can be calculated for the ion. As will be discussed later, there are a wide variety of techniques for ionizing and detecting compounds.

Limitations of MS generally stem from compounds that are not easily ionizable, or which decompose upon ionization. Geometric isomers can generally be distinguished easily, but differences in chirality are not easily resolved. Complications can also arise from samples which are not easily dissolved in common solvents.

3.11.1.2 Ionization techniques

3.11.1.2.1 Electron impact (EI)

In electron impact ionization, a vaporized sample is passed through a beam of electrons. The high energy (typically 70 eV) beam strips electrons from the sample molecules leaving a positively charged radical species. The molecular ion is typically unstable and undergoes decomposition or rearrangement to produce fragment ions. Because of this, electron impact is classified as a “hard” ionization technique. With regards to metal-containing compounds, fragments in EI will almost always contain the metal atom (i.e., $[\text{ML}_n]^{+\bullet}$ fragments to $[\text{ML}_{n-1}]^+ + \text{L}^\bullet$, not $\text{ML}_{n-1}^\bullet + \text{L}^+$). One of the main limitations of EI is that the sample must be volatile and thermally stable.

3.11.1.2.2 Chemical ionization (CI)

In chemical ionization, the sample is introduced to a chamber filled with excess reagent gas (such as methane). The reagent gas is ionized by electrons, forming a plasma with species such as CH_5^+ , which react with the sample to form the pseudomolecular ion $[\text{M}+\text{H}]^+$. Because CI does not involve radical reactions, fragmentation of the sample is generally much lower than that of EI. CI can also be operated in negative mode (to generate anions) by using different reagent gases. For example, a mixture of CH_4 and NO_2 will generate hydroxide ions, which can abstract protons to yield the $[\text{M}-\text{H}]^-$ species. A related technique, atmospheric pressure chemical ionization (APCI) delivers the sample as a neutral spray, which is then ionized by corona discharge, producing ions in a similar manner as described above. APCI is particularly suited for low molecular weight, nonpolar species that cannot be easily analyzed by other common techniques such as ESI.

3.11.1.2.3 Field ionization/desorption

Field ionization and desorption are two closely related techniques which use quantum tunneling of electrons to generate ions. Typically, a highly positive potential is applied to an electrode with a sharp point, resulting in a high potential gradient at the tip (Figure 3.167). As the sample reaches this field, electron tunneling occurs to generate the cation, which is repelled into the mass analyzer. Field ionization utilizes gaseous samples

³¹This content is available online at <<http://cnx.org/content/m38353/1.1/>>.

whereas in field desorption the sample is adsorbed directly onto the electrode. Both of these techniques are *soft*, resulting in low energy ions which do not easily fragment.

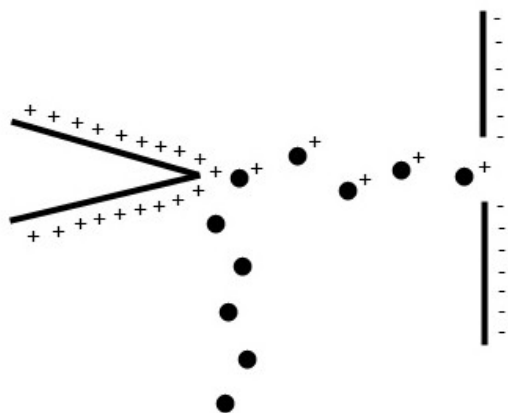


Figure 3.167: Schematic of field ionization.

3.11.1.2.4 Electrospray ionization (ESI)

In ESI, a highly charged aerosol is generated from a sample in solution. As the droplets shrink due to evaporation, the charge density increases until a *coulombic explosion* occurs, producing daughter droplets that repeat the process until individualized sample ions are generated (Figure 3.168). One of the limitations of ESI is the requirement that the sample be soluble. ESI is best applied to charged, polar, or basic compounds.

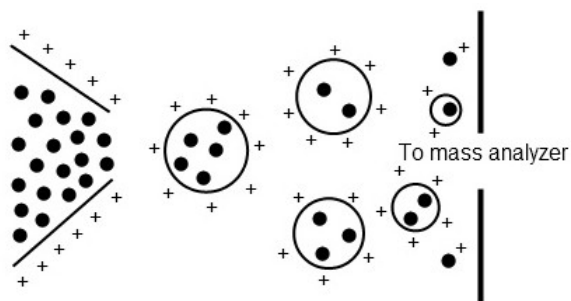


Figure 3.168: Schematic of electrospray ionization.

3.11.1.2.5 Matrix assisted laser desorption ionization (MALDI)

Laser desorption ionization generates ions by ablation from a surface using a pulsed laser. This technique is greatly improved by the addition of a matrix co-crystallized with the sample. As the sample is irradiated, a plume of desorbed molecules is generated. It is believed that ionization occurs in this plume due to a variety of chemical and physical interactions between the sample and the matrix (Figure 3.169). One of the major advantages of MALDI is that it produces singly charged ions almost exclusively and can be used to volatilize extremely high molecular weight species such as polymers and proteins. A related technique, desorption ionization on silicon (DIOS) also uses laser desorption, but the sample is immobilized on a porous silicon surface with no matrix. This allows the study of low molecular weight compounds which may be obscured by matrix peaks in conventional MALDI.

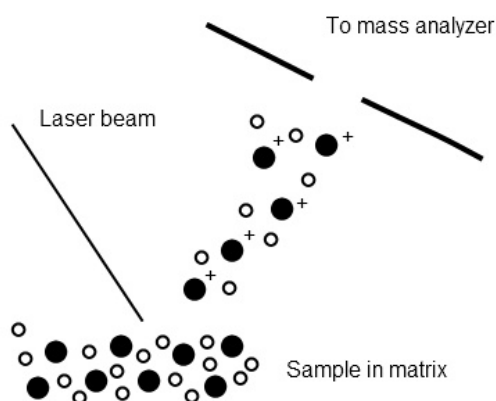


Figure 3.169: Schematic of matrix assisted laser desorption ionization.

3.11.1.2.6 Inductively coupled plasma mass spectrometry (ICP-MS)

A plasma torch generated by electromagnetic induction is used to ionize samples. Because the effective temperature of the plasma is about 10,000 °C, samples are broken down to ions of their constituent elements. Thus, all chemical information is lost, and the technique is best suited for elemental analysis. ICP-MS is typically used for analysis of trace elements.

3.11.1.2.7 Fast atom bombardment (FAB) and secondary ion mass spectrometry (SIMS)

Both of these techniques involve sputtering a sample to generate individualized ions; FAB utilizes a stream of inert gas atoms (argon or xenon) whereas SIMS uses ions such as Cs^+ . Ionization occurs by charge transfer between the ions and the sample or by protonation from the matrix material (Figure 3.170). Both solid and liquid samples may be analyzed. A unique aspect of these techniques for analysis of solids is the ability to do depth profiling because of the destructive nature of the ionization technique.

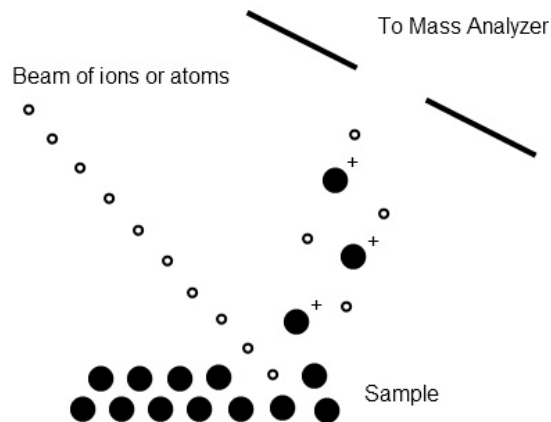


Figure 3.170: Schematic of fast atom bombardment ionization.

3.11.1.2.8 Choosing an ionization technique

Depending on the information desired from mass spectrometry analysis, different ionization techniques may be desired. For example, a hard ionization method such as electron impact may be used for a complex molecule in order to determine the component parts by fragmentation. On the other hand, a high molecular weight sample of polymer or protein may require an ionization method such as MALDI in order to be volatilized. Often, samples may be easily analyzed using multiple ionization methods, and the choice is simplified to choosing the most convenient method. For example, electrospray ionization may be easily coupled to liquid chromatography systems, as no additional sample preparation is required. Table 3.22 provides a quick guide to ionization techniques typically applied to various types of samples.

Information desired	Ionization technique
Elemental analysis	Inductively coupled plasma
Depth profiling	Fast atom bombardment/secondary ion mass spectroscopy
Chemical speciation/component analysis (fragmentation desired)	Electron impact
Molecular species identification of compounds soluble in common solvents	Electrospray ionization
<i>continued on next page</i>	

Molecular species identification of hydrocarbon compounds	Field ionization
Molecular species identification of high molecular weight compounds	Matrix assisted laser desorption ionization
Molecular species identification of halogen containing compounds	Chemical ionization (negative mode)

Table 3.22: Strengths of various ionization techniques.

3.11.1.3 Mass analyzers

3.11.1.3.1 Sectors

A magnetic or electric field is used to deflect ions into curved trajectories depending on the m/z ratio, with heavier ions experiencing less deflection (Figure 3.171). Ions are brought into focus at the detector slit by varying the field strength; a mass spectrum is generated by scanning field strengths linearly or exponentially. Sector mass analyzers have high resolution and sensitivity, and can detect high mass ranges, but are expensive, require large amounts of space, and are incompatible with the most popular ionization techniques MALDI and ESI.

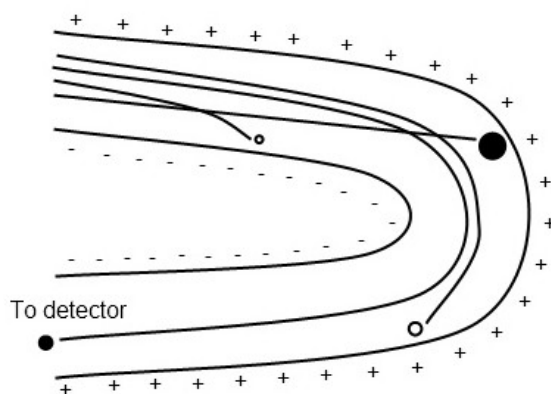


Figure 3.171: Schematic of a magnetic sector mass analyzer.

3.11.1.3.2 Time-of-flight (TOF)

The amount of time required for an ion to travel a known distance is measured (Figure 3.172). A pulse of ions is accelerated through an electric analyzer such that they have identical kinetic energies. As a result, their velocity is directly dependent on their mass. Extremely high vacuum conditions are required to extend the mean free path of ions and avoid collisions. TOF mass analyzers are fastest, have unlimited mass ranges, and allow simultaneous detection of all species, but are best coupled with pulsed ionization sources such as MALDI.

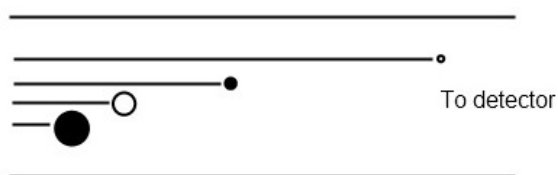


Figure 3.172: Schematic of a time-of-flight (TOF) mass analyzer.

3.11.1.3.3 Quadrupole

Ions are passed through four parallel rods which apply a varying voltage and radiofrequency potential (Figure 3.173). As the field changes, ions respond by undergoing complex trajectories. Depending on the applied voltage and RF frequencies, only ions of a certain m/z ratio will have stable trajectories and pass through the analyzer. All other ions will be lost by collision with the rods. Quadrupole analyzers are relatively inexpensive, but have limited resolution and low mass range.

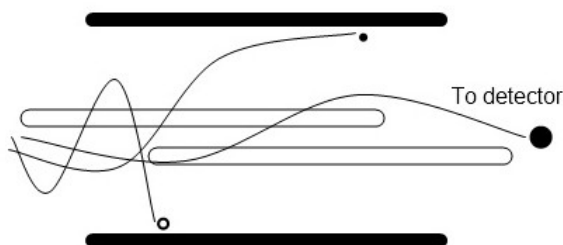


Figure 3.173: Schematic of a quadrupole mass analyzer.

3.11.1.3.4 Ion trap

Ion traps operate under the same principle as quadrupole, but contain the ions in space. Electrodes can be manipulated to selectively eject ions of desired m/z ratios, allowing for mass analysis. Ion traps are uniquely suited for repeated cycles of mass spectrometry because of their ability to retain ions of desired m/z ratios. Selected fragments can be further fragmented by collision induced dissociation with helium gas. Ion traps are compact, relatively inexpensive, and can be adapted to many hybrid instruments.

3.11.1.4 Coupling mass spectrometry to other instruments

Mass spectrometry is a powerful tool for identification of compounds, and is frequently combined with separation techniques such as liquid or gas chromatography for rapid identification of the compounds within

a mixture. Typically, liquid chromatography systems are paired with ESI-quadrupole mass spectrometers to take advantage of the solvated sample. GC-MS systems usually employ electron impact ionization and quadrupole or ion trap mass analyzers to take advantage of the gas-phase molecules and fragmentation libraries associated with EI for rapid identification.

Mass spectrometers are also often coupled in tandem to form MS-MS systems. Typically the first spectrometer utilizes a hard ionization technique to fragment the sample. The fragments are passed on to a second mass analyzer where they may be further fragmented and analyzed. This technique is particularly important for studying large, complex molecules such as proteins.

3.11.1.5 Bibliography

- W. Henderson and J. S. McIndoe, *Mass Spectrometry of Inorganic, Coordination, and Organometallic Compounds*, John Wiley & Sons Ltd., Chichester (2005).
- *Inorganic Mass Spectrometry Fundamentals and Applications*, Ed. C. M. Barshick, D. C. Duckworth, and D. H. Smith, Marcel Dekker Inc., New York (2000).
- F. W. McLafferty, *Science*, 1981, **214**, 280.

Solutions to Exercises in Chapter 3

Solution to Exercise 3.7.3.1 (p. 335)

Using frequency data:

Frequency of peak f - frequency of peak g = 74.82 Hz - 67.76 Hz = 7.06 Hz

Frequency of peak e - frequency of peak f = 81.88 Hz - 74.82 Hz = 7.06 Hz

Average = 7.06 Hz

$\therefore J(\text{H-H}) = 7.06 \text{ Hz}$

Alternatively, using chemical shift data:

Chemical shift of peak f - chemical shift of peak g = 1.2470 ppm - 1.1293 ppm = 0.1177 ppm

Chemical shift of peak e - chemical shift of peak f = 1.3646 ppm - 1.2470 ppm = 0.1176 ppm

Average = 0.11765 ppm

0.11765 ppm x 60 MHz = 7.059 Hz

$\therefore J(\text{H-H}) = 7.06 \text{ Hz}$

Notice the coupling constant for this multiplet is the same as that in the example. This is to be expected since the two multiplets are coupled with each other.

Chapter 4

Reactions Kinetics and Pathways

4.1 Dynamic Headspace Gas Chromatography Analysis¹

4.1.1 Introduction

Gas chromatography (GC) is a very commonly used chromatography in analytic chemistry for separating and analyzing compounds that are gaseous or can be vaporized without decomposition. Because of its simplicity, sensitivity, and effectiveness in separating components of mixtures, gas chromatography is an important tools in chemistry. It is widely used for quantitative and qualitative analysis of mixtures, for the purification of compounds, and for the determination of such thermochemical constants as heats of solution and vaporization, vapor pressure, and activity coefficients. Compounds are separated due to differences in their partitioning coefficient between the stationary phase and the mobile gas phase in the column.

4.1.2 Physical components of a GC system

A gas chromatograph (Figure 4.1) consists of a carrier gas system, a sampling system, a separation system, a detection system, and a data recording system.

¹This content is available online at <<http://cnx.org/content/m34622/1.1/>>.

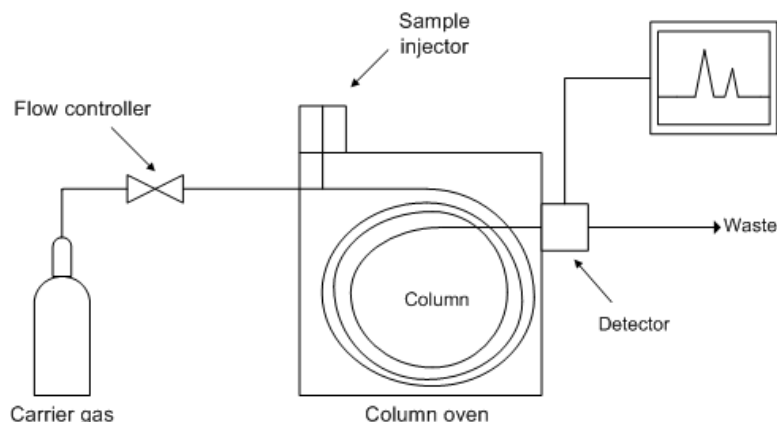


Figure 4.1: Physical components of a typical GC system.

4.1.2.1 Carrier gas system

The carrier gas system consists of carrier gas sources, purification, and gas flow control. The carrier gas must be chemically inert. Commonly used gases include nitrogen, helium, argon, and carbon dioxide. The choice of carrier gas often depends upon the type of detector used. A molecular sieve is often contained in the carrier gas system to remove water and other impurities.

4.1.2.2 Auto sampling system

An auto sampling system consists of auto sampler, and vaporization chamber. The sample to be analyzed is loaded at the injection port via a hypodermic syringe and it will be volatilized as the injection port is heated up. Typically samples of one micro liter or less are injected on the column. These volumes can be further reduced by using what is called a split injection system in which a controlled fraction of the injected sample is carried away by a gas stream before entering the column.

4.1.2.3 Separation system

The separation system consists of columns and temperature controlling oven. The column is where the components of the sample are separated, and is the crucial part of a GC system. The column is essentially a tube that contains different stationary phases have different partition coefficients with analytes, and determine the quality of separation. There are two general types of column: packed (Figure 4.2) and capillary also known as open tubular (Figure 4.3).

- Packed columns contain a finely divided, inert, solid support material coated with liquid stationary phase. Most packed columns are 1.5 – 10 m in length and have an internal diameter of 2 – 4 mm.
- Capillary columns have an internal diameter of a few tenths of a millimeter. They can be one of two types; wall-coated open tubular (WCOT) or support-coated open tubular (SCOT). Wall-coated columns consist of a capillary tube whose walls are coated with liquid stationary phase. In support-coated columns, the inner wall of the capillary is lined with a thin layer of support material such as diatomaceous earth, onto which the stationary phase has been adsorbed. SCOT columns are generally less efficient than WCOT columns. Both types of capillary column are more efficient than packed columns.



Figure 4.2: An example of a packed GC column.



Figure 4.3: An example of a capillary column.

4.1.2.4 Detectors

The purpose of a detector is to monitor the carrier gas as it emerges from the column and to generate a signal in response to variation in its composition due to eluted components. As it transmits physical signal

into recordable electrical signal, it is another crucial part of GC. The requirements of a detector for GC are listed below.

Detectors for GC must respond rapidly to minute concentration of solutes as they exit the column, i.e., they are required to have a fast response and a high sensitivity. Other desirable properties of a detector are: linear response, good stability, ease of operation, and uniform response to a wide variety of chemical species or, alternatively predictable and selective response to one or more classes of solutes.

4.1.2.5 Recording devices

GC system originally used paper chart readers, but modern system typically uses an online computer, which can track and record the electrical signals of the separated peaks. The data can be later analyzed by software to provide the information of the gas mixture.

4.1.3 How does GC work?

4.1.3.1 Separation terminology

An ideal separation is judged by resolution, efficiency, and symmetry of the desired peaks, as illustrated by Figure 4.4.

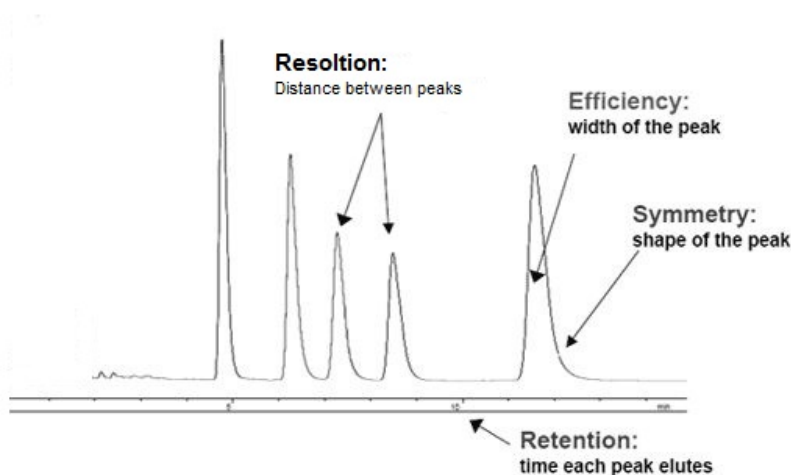


Figure 4.4: Separation terminology.

4.1.3.1.1 Resolution (R)

Resolution can be simply expressed as the distance on the output trace between two peaks. The highest possible resolution is the goal when developing a separation method. Resolution is defined by the R value, (4.1), which can be expressed mathematically, (4.2), where k is capacity, α is selectivity, and N is the number of theoretical plates. An R value of 1.5 is defined as being the minimum required for baseline separation,

i.e., the two adjacent peaks are separated by the baseline. Separation for different R values is illustrated in Figure 4.5.

$$R = \text{capacity} \times \text{selectivity} \times \text{efficiency} \quad (4.1)$$

$$R = [k/(1+k)](\alpha - 1/\alpha)(N^{0.5}/4) \quad (4.2)$$

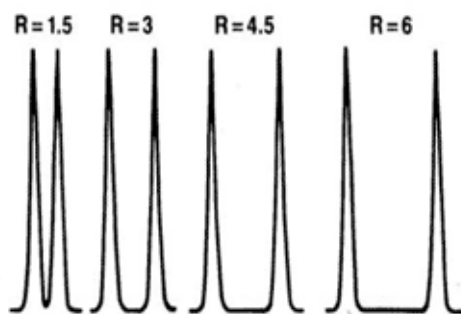


Figure 4.5: Different separation resolutions.

4.1.3.1.2 Capacity (k')

Capacity (k') is known as the retention factor. It is a measure of retention by the stationary phase. It is calculated from (4.3), where t_r = retention time of analyte (substance to be analyzed), and t_m = retention time of an unretained compound.

$$k' = (t_r - t_m)/t_m \quad (4.3)$$

4.1.3.1.3 Selectivity

Selectivity is related to α , the separation factor (Figure 4.6). The value of α should be large enough to give baseline resolution, but minimized to prevent waste.

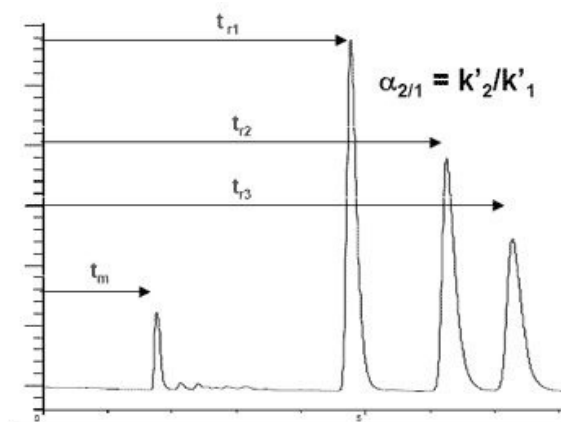


Figure 4.6: Scheme for the calculation of selectivity.

4.1.3.1.4 Efficiency

Narrow peaks have high efficiency (Figure 4.7), and are desired. Units of efficiency are "theoretical plates" (N) and are often used to describe column performance. "Plates" is the current common term for N , is defined as a function of the retention time (t_r) and the full peak width at half maximum ($W_{b1/2}$), EQ.

$$N = 5.545 (t_r/W_{b1/2})^2 \quad (4.4)$$

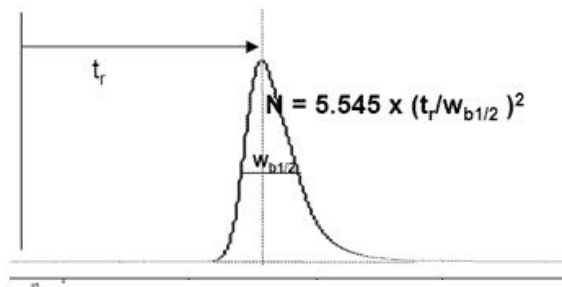


Figure 4.7: Scheme for calculating efficiency.

4.1.3.1.5 Peak symmetry

The symmetry of a peak is judged by the values of two half peak widths, a and b (Figure 4.8). When $a = b$, a peak is called symmetric, which is desired. Unsymmetrical peaks are often described as "tailing" or

"fronting".

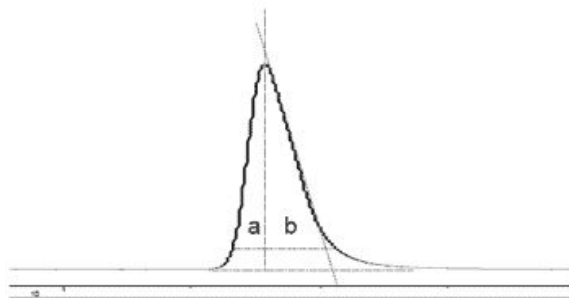


Figure 4.8: Scheme for the symmetry of a peak.

4.1.3.1.6 An ideal separation

The attributions of an ideal separation are as follows:

- Should meet baseline resolution of the compounds of interest.
- Each desired peak is narrow and symmetrical.
- Has no wasted dead time between peaks.
- Takes a minimal amount of time to run.
- The result is reproducible.

4.1.3.2 How does GC work?

In its simplest form gas chromatography is a process whereby a sample is vaporized and injected onto the chromatographic column, where it is separated into its many components. The elution is brought about by the flow of carrier gas (Figure 4.9). The carrier gas serves as the mobile phase that elutes the components of a mixture from a column containing an immobilized stationary phase. In contrast to most other types of chromatography, the mobile phase does not interact with molecules of the analytes. Carrier gases, the mobile phase of GC, include helium, hydrogen and nitrogen which are chemically inert. The stationary phase in gas-solid chromatography is a solid that has a large surface area at which adsorption of the analyte species (solutes) take place. In gas-liquid chromatography, a stationary phase is liquid that is immobilized on the surface of a solid support by adsorption or by chemical bonding.

Gas chromatographic separation occurs because of differences in the positions of adsorption equilibrium between the gaseous components of the sample and the stationary phases (Figure 4.9). In GC the distribution ratio (ratio of the concentration of analytes in stationary and mobile phase) is dependent on the component vapor pressure, the thermodynamic properties of the bulk component band and affinity for the stationary phase. The equilibrium is temperature dependent. Hence the importance of the selection the stationary phase of the column and column temperature programming in optimizing a separation.

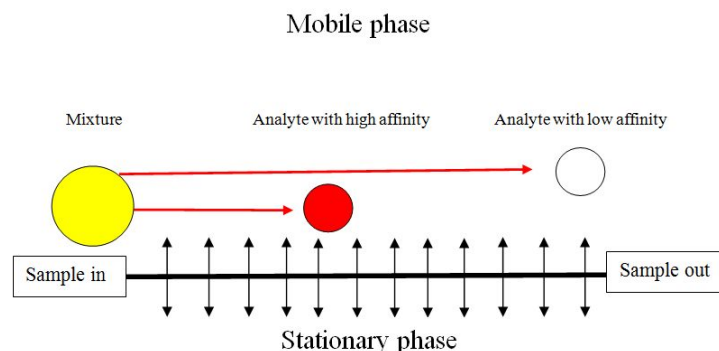


Figure 4.9: Scheme for partition in mobile and stationary phases.

4.1.3.3 Choice of method

4.1.3.3.1 Carrier gas and flow rate

Helium, nitrogen, argon, hydrogen and air are typically used carrier gases. Which one is used is usually determined by the detector being used, for example, a discharge ionization detection (DID) requires helium as the carrier gas. When analyzing gas samples, however, the carrier is sometimes selected based on the sample's matrix, for example, when analyzing a mixture in argon, an argon carrier is preferred, because the argon in the sample does not show up on the chromatogram. Safety and availability are other factors, for example, hydrogen is flammable, and high-purity helium can be difficult to obtain in some areas of the world.

The carrier gas flow rate affects the analysis in the same way that temperature does. The higher the flow rate the faster the analysis, but the lower the separation between analytes. Furthermore, the shape of peak will be also effected by the flow rate. The slower the rate is, the more axial and radical diffusion are, the broader and the more asymmetric the peak is. Selecting the flow rate is therefore the same compromise between the level of separation and length of analysis as selecting the column temperature.

4.1.3.3.2 Column Selection

Table 4.1 shows commonly used stationary phase in various applications.

Stationary phase	Common trade name	Maximum temperature (°C)	Common applications
<i>continued on next page</i>			

Polydimethyl siloxane	OV-1, SE-30	350	General-purpose non-polar phase, hydrocarbons, polynuclear aromatics, drugs, steroids, PCBs
Poly(phenylmethyl-dimethyl) siloxane (10% phenyl)	OV-3, SE-52	350	Fatty acid methyl esters, alkaloids, drugs, halogenated compounds
Poly(phenylmethyl) siloxane (50% phenyl)	OV-17	250	Drugs, steroids, pesticides, glycols
Poly(trifluoropropyl-dimethyl) siloxane	OV-210	200	Chlorinated aromatics, nitroaromatics, alkyl-substituted benzenes
Polyethylene glycol	Carbowax 20M	250	Free acids, alcohols, ethers, essential oils, glycols
Poly(dicyanoallyldimethyl) siloxane	OV-275	240	Polyunsaturated fatty acid, rosin acids, free acids, alcohols

Table 4.1: Some common stationary phases for gas-liquid chromatography.

4.1.3.3.3 Column temperature and temperature program

For precise work, the column temperature must be controlled to within tenths of a degree. The optimum column temperature is dependent upon the boiling point of the sample. As a rule of thumb, a temperature slightly above the average boiling point of the sample results in an elution time of 2 - 30 minutes. Minimal temperatures give good resolution, but increase elution times. If a sample has a wide boiling range, then temperature programming can be useful. The column temperature is increased (either continuously or in steps) as separation proceeds. Another effect that temperature may have is on the shape of peak as flow rate does. The higher the temperature is, the more intensive the diffusion is, the worse the shape is. Thus, a compromise has to be made between goodness of separation and retention time as well as peak shape.

4.1.3.3.4 Detector selection

A number of detectors are used in gas chromatography. The most common are the flame ionization detector (FID) and the thermal conductivity detector (TCD). Both are sensitive to a wide range of components, and both work over a wide range of concentrations. While TCDs are essentially universal and can be used to detect any component other than the carrier gas (as long as their thermal conductivities are different from that of the carrier gas, at detector temperature), FIDs are sensitive primarily to hydrocarbons, and are more sensitive to them than TCD. However, an FID cannot detect water. Both detectors are also quite robust. Since TCD is non-destructive, it can be operated in-series before an FID (destructive), thus providing complementary detection of the same analytes. For halides, nitrates, nitriles, peroxides, anhydrides and organometallics, ECD is a very sensitive detection, which can detect up to 50 fg of those analytes. Different types of detectors are listed below in Table 4.2, along with their properties.

Detector	Type	Support gases	Selectivity	Detectability	Dynamic range
Flame ionization (FID)	Mass flow	Mass flow	Most organic compounds	100 pg	10^7
Thermal conductivity (TCD)	Concentration	Reference	Universal	1 ng	10^7
Electron capture (ECD)	Concentration	Make-up	Halides, nitrates, nitriles, peroxides, anhydrides, organometallics	50 fg	10^5
Nitrogen-phosphorus	Mass flow	Hydrogen and air	Nitrogen, phosphorus	10 pg	10^6
Flame photometric (FPD)	Mass flow	Hydrogen and air possibly oxygen	Sulphur, phosphorus, tin, boron, arsenic, germanium, selenium, chromium	100 pg	10^3
Photo-ionization (PID)	Concentration	Make-up	Aliphatics, aromatics, ketones, esters, aldehydes, amines, heterocyclics, organosulphurs, some organometallics	2 pg	10^7
<i>continued on next page</i>					

Hall electrolytic conductivity	elec-con-	Mass flow	Hydrogen, oxygen	Halide, nitrogen, nitrosamine, sulphur	ni-ni-	-	-
--------------------------------	-----------	-----------	------------------	--	--------	---	---

Table 4.2: Different types of detectors and their properties.

4.1.4 Headspace analysis using GC

Most consumer products and biological samples are composed of a wide variety of compounds that differ in molecular weight, polarity, and volatility. For complex samples like these, headspace sampling is the fastest and cleanest method for analyzing volatile organic compounds. A headspace sample is normally prepared in a vial containing the sample, the dilution solvent, a matrix modifier, and the headspace (Figure 4.10). Volatile components from complex sample mixtures can be extracted from non-volatile sample components and isolated in the headspace or vapor portion of a sample vial. An aliquot of the vapor in the headspace is delivered to a GC system for separation of all of the volatile components.

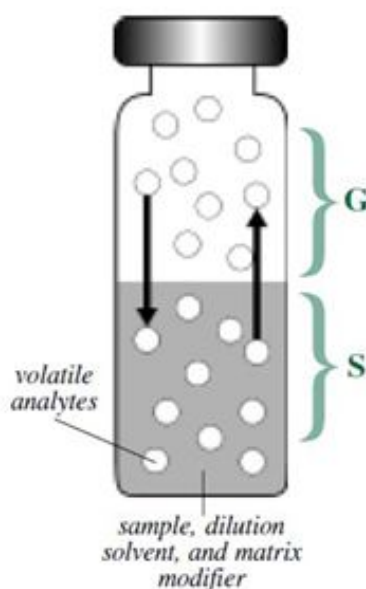


Figure 4.10: Schematic representation of the phases of the headspace in the vial. Adapted from *A Technical Guide for Static Headspace Analysis Using GC*, Restek Corp. (2000).

The gas phase (G in Figure 4.10) is commonly referred to as the headspace and lies above the condensed sample phase. The sample phase (S in Figure 4.10) contains the compound(s) of interest and is usually in the form of a liquid or solid in combination with a dilution solvent or a matrix modifier. Once the sample phase is introduced into the vial and the vial is sealed, volatile components diffuse into the gas phase until the headspace has reached a state of equilibrium as depicted by the arrows. The sample is then taken from the headspace.

4.1.4.1 Basic principles of headspace analysis

4.1.4.1.1 Partition coefficient

Samples must be prepared to maximize the concentration of the volatile components in the headspace, and minimize unwanted contamination from other compounds in the sample matrix. To help determine the concentration of an analyte in the headspace, you will need to calculate the partition coefficient (K), which is defined by (4.5), where C_s is the concentration of analyte in sample phase and C_g is the concentration of analyte in gas phase. Compounds that have low K values will tend to partition more readily into the gas phase, and have relatively high responses and low limits of detection. K can be lowered by changing the temperature at which the vial is equilibrated or by changing the composition of the sample matrix.

$$K = C_s/C_g \quad (4.5)$$

4.1.4.1.2 Phase ratio

The phase ratio (β) is defined as the relative volume of the headspace compared to volume of the sample in the sample vial, (4.6), where V_s =volume of sample phase and V_g =volume of gas phase. Lower values for β (i.e., larger sample size) will yield higher responses for volatile compounds. However, decreasing the β value will not always yield the increase in response needed to improve sensitivity. When β is decreased by increasing the sample size, compounds with high K values partition less into the headspace compared to compounds with low K values, and yield correspondingly smaller changes in C_g . Samples that contain compounds with high K values need to be optimized to provide the lowest K value before changes are made in the phase ratio.

$$\beta = V_g/V_s \quad (4.6)$$

4.1.5 Bibliography

- D. L. Pavia, G. M. Lampman, G. S. Kriz, and R. G. Engel, *Introduction to Organic Laboratory Techniques*, 4th ed. Thomson Brooks/Cole (2006).
- D. C. Harris, *Quantitative Chemical Analysis*, 5th ed., Freeman and Company (1999).
- M. O. Nutt, J. B. Hughes, and M. S. Wong, *Environ. Sci. Technol.*, 2005, **39**, 1346.

4.2 Gas Chromatography Analysis of the Hydrodechlorination Reaction of Perchloroethylene ²

4.2.1 Introduction

Perchloroethylene (PCE, FIGURE) is a widely spread environmental contaminant and a member of the class of compounds known as dense non-aqueous phase liquids (DNAPLs). Palladium-on-gold nanoparticles (Pd/Au NPs) have shown high activities for the hydrodechlorination (HDC) of chlorinated compounds.

²This content is available online at <<http://cnx.org/content/m34634/1.1/>>.

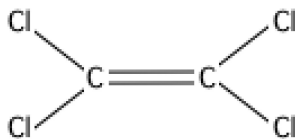


Figure 4.11: Perchloroethylene (PCE).

To quantify the reaction rate, a 250 mL screw-cap bottle with 77 mL of headspace gas was used as the batch reactor for the studies. PCE (3 μL) is added in 173 mL DI water purged with hydrogen gas for 15 mins, together with 0.2 μL pentane as internal standard. Dynamic headspace analysis using GC has been applied. The experimental condition is concluded in the table below (Table 4.3).

PCE	3 μL
H ₂	1.5 ppm
pentane	0.2 μL
DI water	173 mL
60% 4 nm Pd/Au NP solution ^a	842 μL
Temperature	25 °C
Pressure	1 atm
Reaction time	1 h

Table 4.3: The experimental condition in HDC of PCE. ^a 60% 4nm Pd/Au NP refers to 60% monolayer Pd surface coverage on 4 nm Au nanoparticles. The amount of Pd in the added solution is 5.76×10^{-6} g.

4.2.2 Reaction kinetics

First order reaction is assumed in the HDC of PCE, (4.7), where K_{means} is defined by (4.8), and C_{cat} is equal to the concentration of Pd metal within the reactor and k_{cat} is the reaction rate with units of $\text{L/g}_{\text{Pd}}/\text{min}$.

$$-dC_{\text{PCE}}/dt = k_{\text{meas}} \times C_{\text{PCE}} \quad (4.7)$$

$$k_{\text{meas}} = k_{\text{cat}} \times C_{\text{cat}} \quad (4.8)$$

4.2.3 The GC method

The GC methods used are listed in Table 4.4.

GC type	Agilent 6890N GC
Column	Supelco 1-2382 40/60 Carboxen-1000 packed column
Detector	FID
Oven temperature	210 °C
Flow rate	35 mL/min
Injection amount	200 μ L
Carrier gas	Helium
Detection time	5 min

Table 4.4: GC method for detection of PCE and other related chlorinated compounds.

4.2.4 Quantitative method

Since pentane is introduced as the inert internal standard, the relative concentration of PCE in the system can be expressed as the ratio of area of PCE to pentane in the GC plot, (4.9).

$$C_{\text{PCE}} = (\text{peak area of PCE})/(\text{peak area of pentane}) \quad (4.9)$$

4.2.5 Results and Analysis

As shown in Figure 4.12, the major analytes (referenced as PCE, TCE, pentane, and ethane) are very well separated from each other, allowing for quantitative analysis. The peak areas of the peaks associated with these compounds are integrated by the computer automatically, and are listed in (Table 4.5) with respect to time.

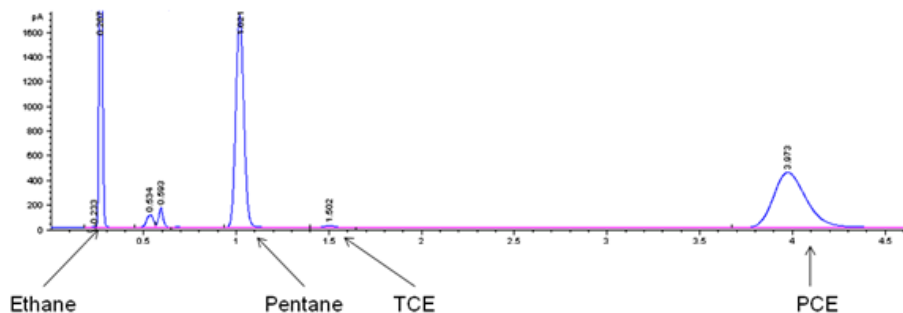


Figure 4.12: An example of a GC plot of a headspace sample for the HDC of PCE.

Time/min	Peak area of pentane	Peak area of PCE	Peak area of TCE
0	5992.93	13464	0
5.92	6118.5	11591	194
11.25	5941.2	8891	321.5
16.92	5873.5	7055.6	316.5
24.13	5808.6	5247.4	279.7
32.65	5805.3	3726.3	222.7
43.65	5949.8	2432.8	154.2
53.53	5567.5	1492.3	97.1
64.72	5725.6	990.2	57.4
77.38	5624.3	550	35.8
94.13	5432.5	225.7	18.73
105	5274.4	176.8	10.26

Table 4.5: Peak area of pentane, PCE, TCE as a function of reaction time.

Normalize PCE concentration with respect to peak area of pentane and then to the initial PCE concentration, and then calculate the nature logarithm of this normalized concentration, as shown in Table 4.6.

Time (min)	PCE/pentane	PCE/pentane/PCE _{initial}	ln(PCE/Pentane/PCE _{initial})
0	2.2466	1.0000	0.0000
5.92	1.8944	0.8432	-0.1705
11.25	1.4965	0.6661	-0.4063
16.92	1.2013	0.5347	-0.6261
24.13	0.9034	0.4021	-0.9110
32.65	0.6419	0.2857	-1.2528
43.65	0.4089	0.1820	-1.7038
53.53	0.2680	0.1193	-2.1261
64.72	0.1729	0.0770	-2.5642
77.38	0.0978	0.0435	-3.1344
94.13	0.0415	0.0185	-3.9904
105	0.0335	0.0149	-4.2050

Table 4.6: Normalized PCE concentration as a function of reaction time.

From a plot normalized PCE concentration against time shows the concentration profile of PCE during reaction (Figure 4.13), while the slope of the logarithmic plot provides the reaction rate constant (k).

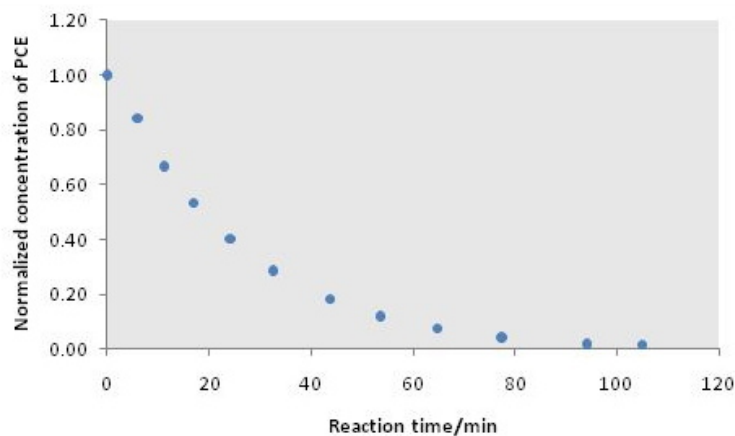


Figure 4.13: A plot of the normalized concentration profile of PCE.

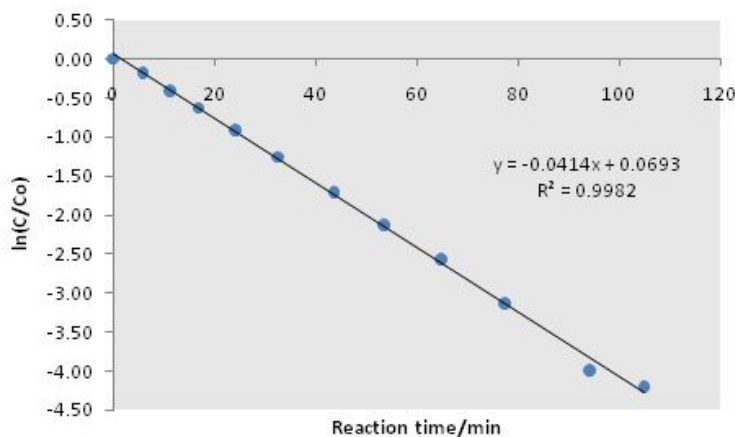


Figure 4.14: A plot of $\ln(C_{\text{PCE}}/C_0)$ versus time.

From Figure 4.13, we can see that the linearity, i.e., the goodness of the assumption of first order reaction, is very much satisfied throughout the reaction. Thus, the reaction kinetic model is validated. Furthermore, the reaction rate constant can be calculated from the slope of the fitted line, i.e., $k_{\text{meas}} = 0.0414 \text{ min}^{-1}$. From this the k_{cat} can be obtained, (4.10).

$$k_{\text{cat}} = k_{\text{meas}}/C_{\text{Pd}} = \frac{0.0414 \text{ min}^{-1}}{(5.76 \times 10^{-6} \text{ g}/0.173 \text{ L})} = 1234 \text{ L/g}_{\text{Pd}}\cdot\text{min} \quad (4.10)$$

4.2.6 Bibliography

- M, O. Nutt, J, B. Hughes, and M, S. Wong, *Environ. Sci. Technol.*, 2005, **39**, 1346.
- *A Technical Guide for Static Headspace Analysis Using GC*, Restek Corp. (2000).

4.3 Temperature-Programmed Desorption Mass Spectroscopy Applied in Surface Chemistry ³

4.3.1 Introduction

The temperature-programmed desorption (TPD) technique is often used to monitor surface interactions between adsorbed molecules and substrate surface. Utilizing the dependence on temperature is able to discriminate between processes with different activation parameters, such as activation energy, rate constant, reaction order and Arrhenius pre-exponential factor. In order to provide an example of the set-up and results from a TPD experiment we are going to use an ultra-high vacuum (UHV) chamber equipped with a quadrupole mass spectrometer to exemplify a typical surface gas-solid interaction and estimate several important kinetic parameters.

4.3.2 Experimental system

4.3.2.1 Ultra-high vacuum (UHV) chamber

When we start to set up an apparatus for a typical surface TPD experiment, we should first think about how we can generate an extremely clean environment for the solid substrate and gas adsorbents. Ultra-high vacuum (UHV) is the most basic requirement for surface chemistry experiments. UHV is defined as a vacuum regime lower than 10^{-9} Torr. At such a low pressure the *mean free path* of a gas molecule is approximately 40 Km, which means gas molecules will collide and react with sample substrate in the UHV chamber many times before colliding with each other, ensuring all interactions take place on the substrate surface.

Most of time UHV chambers require the use of unusual materials in construction and by heating the entire system to $\sim 180^\circ\text{C}$ for several hours baking to remove moisture and other trace adsorbed gases around the wall of the chamber in order to reach the ultra-high vacuum environment. Also, outgas from the substrate surface and other bulk materials should be minimized by careful selection of materials with low vapor pressures, such as stainless steel, for everything inside the UHV chamber. Thus bulk metal crystals are chosen as substrates to study interactions between gas adsorbates and crystal surface itself. Figure 4.15 shows a schematic of a TPD system, while Figure 4.16 shows a typical TPD instrument equipped with a quadrupole MS spectrometer and a reflection absorption infrared spectrometer (RAIRS).

³This content is available online at <<http://cnx.org/content/m38319/1.1/>>.

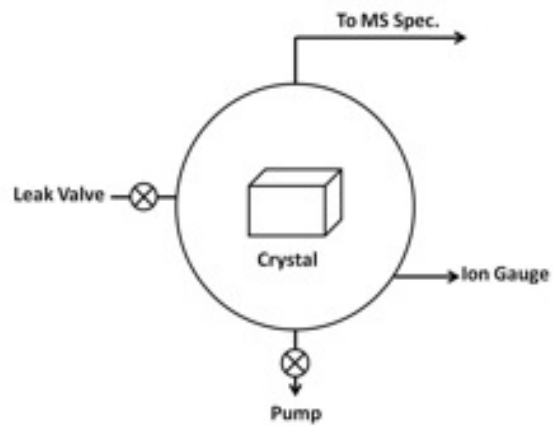


Figure 4.15: Schematic diagram of a TPD apparatus.

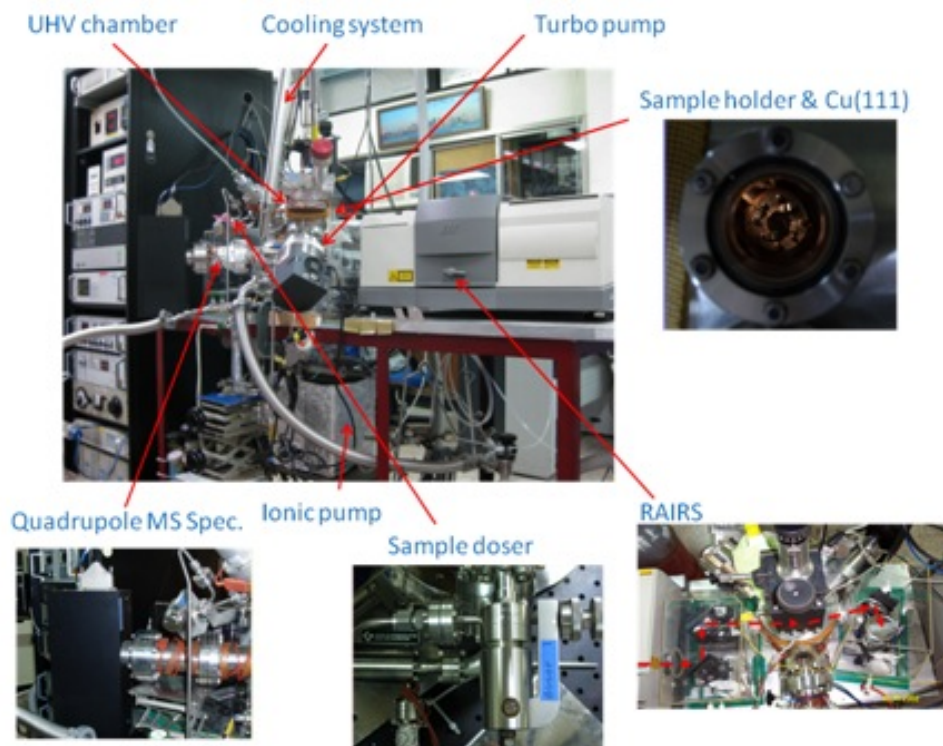


Figure 4.16: A typical TPD apparatus composed of a UHV chamber equipped with a series of pumping systems, cooling system, sample dosing system as well as surface detection instruments including a quadrupole MS Spectrometer and a reflection absorption infra red spectrometer (RAIRS).

4.3.2.2 Pumping system

There is no single pump that can operate all the way from atmospheric pressure to UHV. Instead, a series of different pumps are used, according to the appropriate pressure range for each pump. Pumps are commonly used to achieve UHV include:

- Turbomolecular pumps (turbo pumps).
- Ionic pumps.
- Titanium sublimation pumps.
- Non-evaporate mechanical pumps.

UHV pressures are measured with an ion-gauge, either a hot filament or an inverted magnetron type. Finally, special seals and gaskets must be used between components in a UHV system to prevent even trace leakage. Nearly all such seals are all metal, with knife edges on both sides cutting into a soft (e.g., copper) gasket. This all-metal seal can maintain system pressures down to $\sim 10^{-12}$ Torr.

4.3.2.3 Manipulator and bulk metal crystal

A UHV manipulator (or sample holder, see Figure 4.16) allows an object that is inside a vacuum chamber and under vacuum to be mechanically positioned. It may provide rotary motion, linear motion, or a combination

of both. The manipulator may include features allowing additional control and testing of a sample, such as the ability to apply heat, cooling, voltage, or a magnetic field. Sample heating can be accomplished by thermal radiation. A filament is mounted close to the sample and resistively heated to high temperature. In order to simplify complexity from the interaction between substrate and adsorbates, surface chemistry labs often carry out TPD experiments by choosing a substrate with single crystal surface instead of polycrystalline or amorphous substrates (see Figure 4.15).

4.3.2.4 Pretreatment

Before selected gas molecules are dosed to the chamber for adsorption, substrates (metal crystals) need to be cleaned through argon plasma sputtering, followed by annealing at high temperature for surface reconstruction. After these pretreatments, the system is again cooled down to very low temperature (liquid N₂ temp), which facilitating gas molecules adsorbed on the substrate surface. Adsorption is a process in which a molecule becomes adsorbed onto a surface of another phase. It is distinguished from absorption, which is used when describing uptake into the bulk of a solid or liquid phase.

4.3.2.5 Temperature-programmed desorption processes

After gas molecules adsorption, now we are going to release these adsorbates back into gas phase by programmed-heating the sample holder. A mass spectrometer is set up for collecting these desorbed gas molecules, and then correlation between desorption temperature and fragmentation of desorbed gas molecules will show us certain important information. Figure 4.17 shows a typical TPD experiment carried out by adsorbing CO onto Pd(111) surface, followed by programmed-heating to desorb the CO adsorbates.

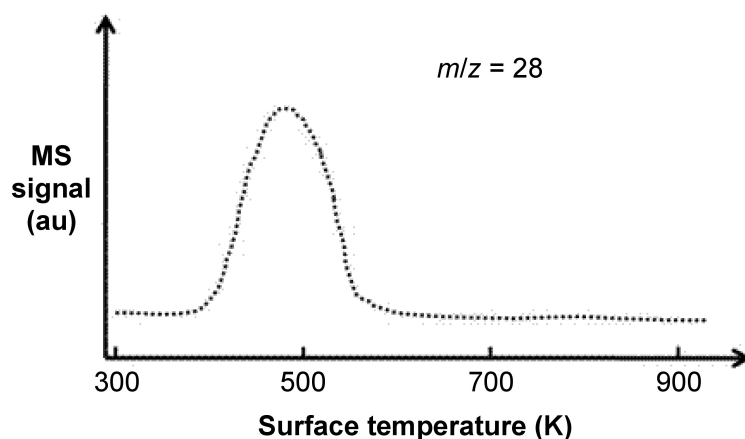


Figure 4.17: MS spectrum taken from a TPD experiment that CO ($m/z = 28$) was first adsorbed on Pd(111) surface, followed by desorbing at a fixed heating rate. The desorption rate which is proportional to the MS signal reaches its maximum around 500 K.

4.3.3 Theory of the TPD experiment

4.3.3.1 Langmuir isotherm

The Langmuir isotherm describes the dependence of the surface coverage of an adsorbed gas on the pressure of the gas above the surface at a fixed temperature. Langmuir isotherm is the simplest assumption, but it provides a useful insight into the pressure dependence of the extent of surface adsorption. It was Irving Langmuir who first studied the adsorption process quantitatively. In his proposed model, he supposed that molecules can adsorb only at specific sites on the surface, and that once a site is occupied by one molecule, it cannot adsorb a second molecule. The adsorption process can be represented as (4.11), where A is the adsorbing molecule, S is the surface site, and A [U+2500]S stands for an A molecule bound to the surface site.



In a similar way, its reverse desorption process can be represented as (4.12).



According to the Langmuir model, we know that the adsorption rate should be proportional to $k_a[A](1-\theta)$, where θ is the fraction of the surface sites covered by adsorbate A. The desorption rate is then proportional to $k_d\theta$. k_a and k_d are the rate constants for the adsorption and desorption. At equilibrium, the rates of these two processes are equal, (4.13) - (4.16). We can replace [A] by P, where P means the gas partial pressure, (4.17).

$$k_a[A](1-\theta) = k_d\theta \quad (4.13)$$

$$\frac{\theta}{1-\theta} = \frac{k_a}{k_d}[A] \quad (4.14)$$

$$K = \frac{k_a}{k_d} \quad (4.15)$$

$$\theta = \frac{K[A]}{1 + K[A]} \quad (4.16)$$

$$\theta = \frac{KP}{1 + KP} \quad (4.17)$$

We can observe the equation above and know that if [A] or P is low enough so that $K[A]$ or $KP \ll 1$, then $\theta \sim K[A]$ or KP , which means that the surface coverage should increase linearly with [A] or P. On the contrary, if [A] or P is large enough so that $K[A]$ or $KP \gg 1$, then $\theta \sim 1$. This behavior is shown in the plot of θ versus [A] or P in Figure 4.18.

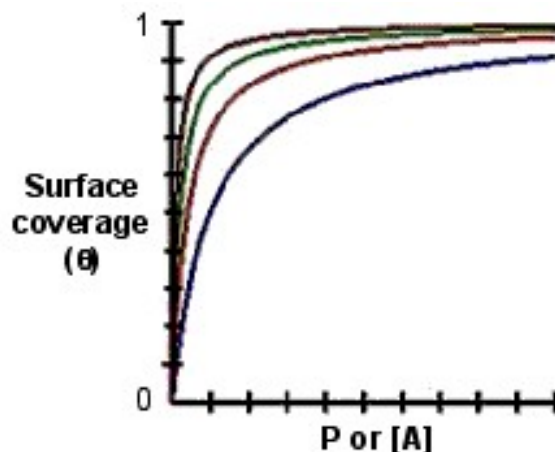


Figure 4.18: Simulated Langmuir isotherms. Value of constant K (k_a/k_d) increases from blue, red, green and brown.

4.3.3.2 Derivation of kinetic parameters based on TPD results

Here we are going to show how to use the TPD technique to estimate desorption energy, reaction energy, as well as Arrhenius pre-exponential factor. Let us assume that molecules are irreversibly adsorbed on the surface at some low temperature T_0 . The leak valve is closed, the valve to the pump is opened, and the “density” of product molecules is monitored with a mass spectrometer as the crystal is heated under programmed temperature (4.18), where β is the heating rate ($\sim 10^\circ\text{C/s}$). We know the desorption rate depends strongly on temperature, so when the temperature of the crystal reaches a high enough value so that the desorption rate is appreciable, the mass spectrometer will begin to record a rise in density. At higher temperatures, the surface will finally become depleted of desorbing molecules; therefore, the mass spectrometer signal will decrease. According to the shape and position of the peak in the mass signal, we can learn about the activation energy for desorption and the Arrhenius pre-exponential factor.

$$T = T_0 + \beta T \quad (4.18)$$

4.3.3.2.1 First-order process

Consider a first-order desorption process (4.19), with a rate constant k_d , (4.20), where A is Arrhenius pre-exponential factor. If θ is assumed to be the number of surface adsorbates per unit area, the desorption rate will be given by (4.21).



$$k_d = A \exp\left(\frac{-\Delta E_a}{RT}\right) \quad (4.20)$$

$$\frac{-d\theta}{dt} = k_d\theta = \theta A \exp\left(\frac{-\Delta E_a}{RT}\right) \quad (4.21)$$

Since we know the relationship between heat rate β and temperature on the crystal surface T , (4.22) and (4.23).

$$T = T_0 + \beta t \quad (4.22)$$

$$\frac{1}{dt} = \frac{\beta}{dT} \quad (4.23)$$

Multiplying by $-d\theta$ gives (4.24), since (4.25) and (4.26). A plot of the form of $-d\theta/dT$ versus T is shown in Figure 4.19.

$$\frac{-d\theta}{dt} = -\beta \frac{d\theta}{dT} \quad (4.24)$$

$$\frac{-d\theta}{dt} = k_d\theta = \theta A \exp\left(\frac{-\Delta E_a}{RT}\right) \quad (4.25)$$

$$\frac{-d\theta}{dT} = \frac{\theta A}{\beta} \exp\left(\frac{-\Delta E_a}{RT}\right) \quad (4.26)$$

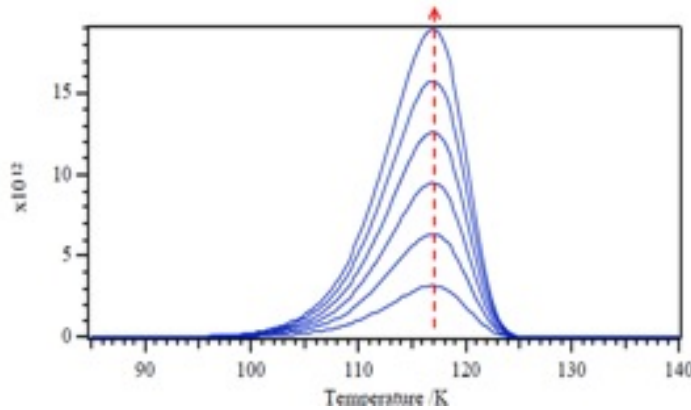


Figure 4.19: A simulated TPD experiment: Consider a first order reaction between adsorbates and surface. Values of T_m keep constant as the initial coverage θ from 1.0×10^{13} to $6.0 \times 10^{13} \text{ cm}^{-2}$. $E_a = 30 \text{ KJ/mol}$; $\beta = 1.5 \text{ }^\circ\text{C/s}$; $A = 1 \times 10^{13}$.

We notice that the T_m (peak maximum) in Figure 4.19 keeps constant with increasing θ , which means the value of T_m does not depend on the initial coverage θ in the first-order desorption. If we want to use different desorption activation energy E_a and see what happens in the corresponding desorption temperature T . We are able to see the T_m values will increase with increasing E_a .

At the peak of the mass signal, the increase in the desorption rate is matched by the decrease in surface concentration per unit area so that the change in $d\theta/dT$ with T is zero: (4.27) - (4.29). Since (4.30), then (4.31) and (4.32).

$$\frac{-d\theta}{dT} = \frac{\theta A}{\beta} \exp\left(\frac{-\Delta E_a}{RT}\right) \quad (4.27)$$

$$\frac{d}{dT} \left[\frac{\theta A}{\beta} \exp\left(\frac{-\Delta E_a}{RT}\right) \right] = 0 \quad (4.28)$$

$$\frac{\Delta E_a}{RT_M^2} = -\frac{1}{\theta} \left(\frac{d\theta}{dT} \right) \quad (4.29)$$

$$-\frac{d\theta}{dT} = \frac{\theta A}{\beta} \exp\left(-\frac{\Delta E_a}{RT}\right) \quad (4.30)$$

$$\frac{\Delta E_a}{RT_M^2} = \frac{A}{\beta} \exp\left(\frac{-\Delta E_a}{RT_M}\right) \quad (4.31)$$

$$2 \ln T_M - \ln \beta = \frac{\Delta E_a}{RT_M} + \ln \frac{\Delta E_a}{RA} \quad (4.32)$$

This tells us if different heating rates β are used and the left-hand side of the above equation is plotted as a function of $1/T_M$, we can see that a straight line should be obtained whose slope is $\Delta E_a/R$ and intercept is $\ln(\Delta E_a/RA)$. So we are able to obtain the activation energy to desorption ΔE_a and Arrhenius pre-exponential factor A .

4.3.3.2.2 Second-order process

Now let consider a second-order desorption process (4.33), with a rate constant k_d . We can deduce the desorption kinetics as (4.34). The result is different from the first-order reaction whose T_m value does not depend upon the initial coverage, the temperature of the peak T_m will decrease with increasing initial surface coverage.



$$-\frac{d\theta}{dT} = A\theta^2 \exp\left(-\frac{\Delta E_a}{RT}\right) \quad (4.34)$$

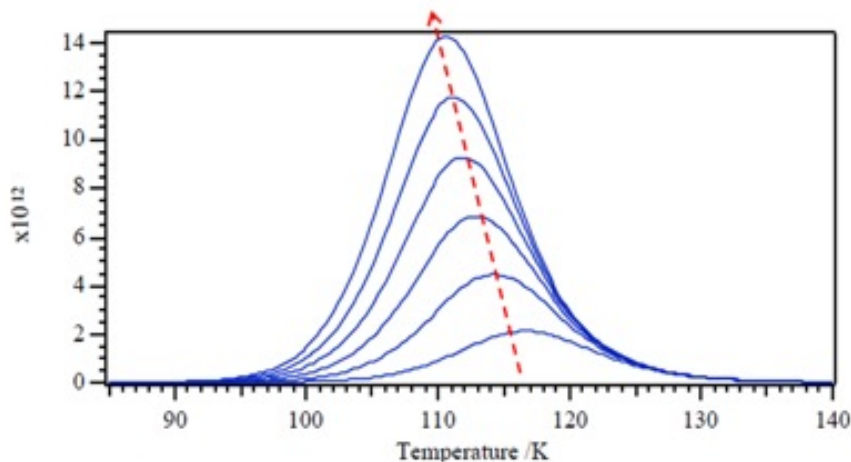


Figure 4.20: A simulated second-order TPD experiment: A second-order reaction between adsorbates and surface. Values of T_m decrease as the initial coverage θ increases from 1.0×10^{13} to $6.0 \times 10^{13} \text{ cm}^{-2}$; $E_a = 30 \text{ KJ/mol}$; $\beta = 1.5 \text{ }^\circ\text{C/s}$; $A = 1 \times 10^{-1}$.

4.3.3.2.3 Zero-order process

The zero-order desorption kinetics relationship as (4.35). Looking at desorption rate for the zero-order reaction (Figure 4.21), we can observe that the desorption rate does not depend on coverage and also implies that desorption rate increases exponentially with T . Also according to the plot of desorption rate versus T , we figure out the desorption rate rapid drop when all molecules have desorbed. Plus temperature of peak, T_m , moves to higher T with increasing coverage θ .

$$-\frac{d\theta}{dT} = A \exp\left(-\frac{\Delta E_a}{RT}\right) \quad (4.35)$$

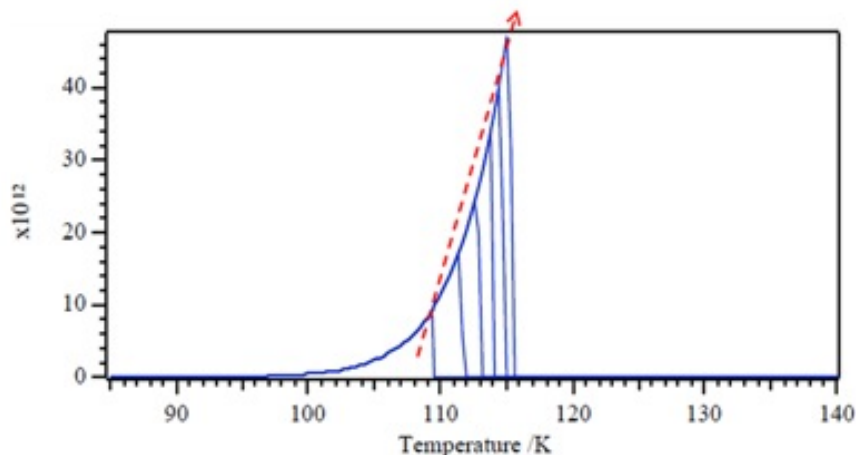


Figure 4.21: A simulated zero-order TPD experiment: A zero-order reaction between adsorbates and surface. Values of T_m increase apparently as the initial coverage θ increases from 1.0×10^{13} to $6.0 \times 10^{13} \text{ cm}^{-2}$; $E_a = 30 \text{ KJ/mol}$; $\beta = 1.5 \text{ }^\circ\text{C/s}$; $A = 1 \times 10^{28}$.

4.3.4 A typical example

A typical TPD spectra of D_2 from Rh(100) for different exposures in Langmuirs ($L = 10^{-6} \text{ Torr-sec}$) shows in Figure 4.22. First we figure out the desorption peaks from g to n show two different desorbing regions. The higher one can undoubtedly be ascribed to chemisorbed D_2 on Rh(100) surface, which means chemisorbed molecules need higher energy used to overcome their activation energy for desorption. The lower desorption region is then due to physisorbed D_2 with much lower desorption activation energy than chemisorbed D_2 . According to the TPD theory we learnt, we notice that the peak maximum shifts to lower temperature with increasing initial coverage, which means it should belong to a second-order reaction. If we have other information about heating rate β and each T_m under corresponding initial surface coverage θ then we are able to calculate the desorption activation energy E_a and Arrhenius pre-exponential factor A .

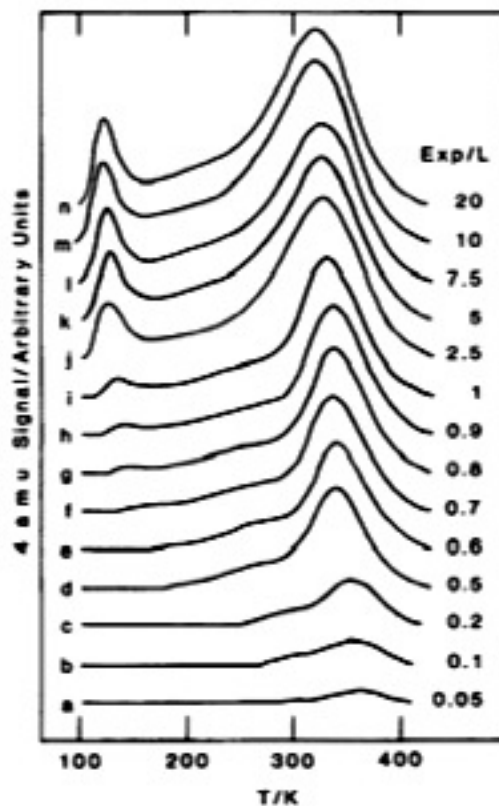


Figure 4.22: TPD spectra of D_2 from Rh(100) for different exposures in L (1 Langmuir = 10^{-6} Torr-s)⁶.

4.3.5 Conclusion

Temperature-programmed desorption is an easy and straightforward technique especially useful to investigate gas-solid interaction. By changing one of parameters, such as coverage or heating rate, followed by running a series of typical TPD experiments, it is possible to obtain several important kinetic parameters (activation energy to desorption, reaction order, pre-exponential factor, etc). Based on the information, further mechanism of gas-solid interaction can be deduced.

4.3.6 Bibliography

- M. N. Roger, An Introduction to Surface Chemistry, <http://www.chem.qmul.ac.uk/surfaces/scc/>⁴
- P. L. Houston, *Chemical Kinetics and Reaction Dynamics*, McGraw Hill, New York (2001).
- I. Langmuir, *J. Am. Chem. Soc.*, 1916, **38**, 221.
- P. A. Redhead, *Vacuum*, 1962, **12**, 203.
- Y. Kim, H. C. Peebles, and J. M. White, *Surface Sci.*, 1982, **114**, 363.

⁴<http://www.chem.qmul.ac.uk/surfaces/scc/>

Chapter 5

Dynamic Processes

5.1 NMR of Dynamic Systems: An Overview ¹

The study of conformational and chemical equilibrium is an important part of understanding chemical species in solution. NMR is one of the most useful and easiest to use tools for such kinds of work. Figure 5.1 shows a pictorial representation of the process of the conformational equilibrium and chemical equilibrium. In both cases if the NMR spectra of the equilibrium species is sufficiently distinct we will have a good chance to use the NMR to investigate the system. In an equilibrium equilibrium system it is the changes in the structure/conformation of the compound that result in the variation of the peaks in the NMR spectrum. The appearance of the spectrum has a lot to do with the rate of the exchange in the equilibrium. Due to the measurement timescale of NMR when the exchange rates are slow two individual sets of peaks are observed. However, for equilibria with fast exchanges an average peak is observed.

NOTE: Chemical equilibrium is defined as the state in which both reactants and products (of a chemical reaction) are present at concentrations which have no further tendency to change with time. Such a state results when the forward reaction proceeds at the same rate (i.e., K_a in Figure 5.1b) as the reverse reaction (i.e., K_d in Figure 5.1b). The reaction rates of the forward and reverse reactions are generally not zero but, being equal, there are no net changes in the concentrations of the reactant and product. This process is called dynamic equilibrium.

NOTE: Conformational isomerism is a form of stereoisomerism in which the isomers can be inter-converted exclusively by rotations about formally single bonds. Conformational isomers are distinct from the other classes of stereoisomers for which interconversion necessarily involves breaking and reforming of chemical bonds. The rotational barrier, or barrier to rotation, is the activation energy required to interconvert rotamers. The equilibrium population of different conformers follows a Boltzmann distribution.

¹This content is available online at <<http://cnx.org/content/m43679/1.1/>>.

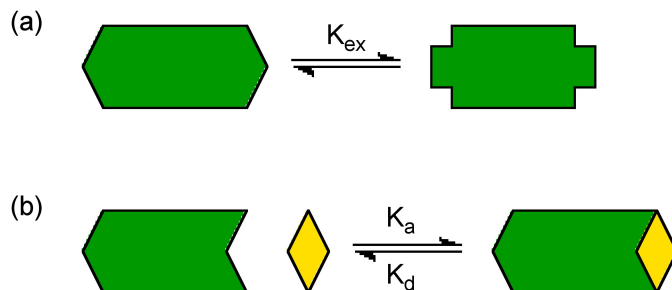


Figure 5.1: The process of (a) conformational equilibrium and (b) chemical equilibrium. Adapted from J. Saad, *Dynamic NMR and Application* (2008), www.microbio.uab.edu/mic774/lectures/Saad-lecture8.pdf.

If we consider a simple system (Figure 5.2) as an example of how to study conformational equilibrium. In this system, the two methyl groups (one is in red, the other blue) will exchange with each other through the rotation of the C-N bond. When the speed of the rotation is fast (faster than the NMR timescale of about 10^{-5} s), NMR can no longer recognize the difference of the two methyl groups, which results in an average peak in the NMR spectrum (as is shown in the red spectrum in Figure 5.3). Conversely, when the speed of the rotation is slowed by cooling (to -50 °C) the two conformations have lifetimes significantly longer that they are observable in the NMR spectrum (as is shown by the dark blue spectrum in Figure 5.3). The changes that occur to this spectrum with varying temperature is shown in Figure 5.3, where it is clearly seen the change of the NMR spectrum with the decreasing of temperature.

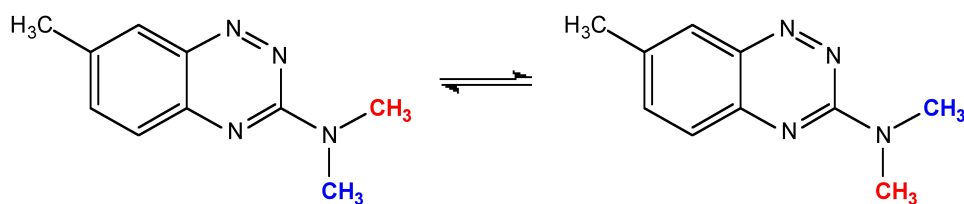


Figure 5.2: An example of a process of a conformational equilibrium.

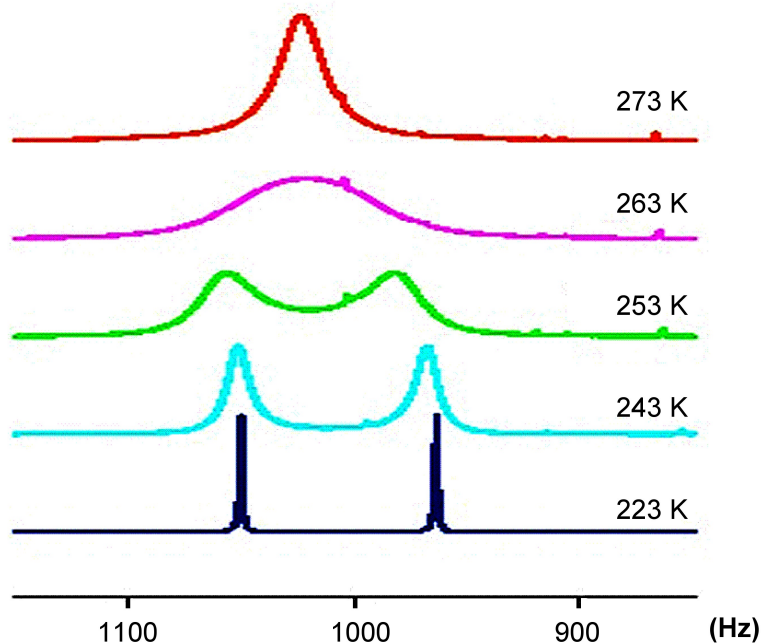


Figure 5.3: The variation of the NMR signal for the amine methyl groups in Figure 5.2 as a function of temperature. Adapted from J. Saad, *Dynamic NMR and Application* (2008), www.microbio.uab.edu/mic774/lectures/Saad-lecture8.pdf.

Based upon the above, it should be clear that the presence of an average or separate peaks can be used as an indicator of the speed of the rotation. As such this technique is useful in probing systems such as molecular motors. One of the most fundamental problems is to confirm that the motor is really rotating, while the other is to determine the rotation speed of the motors. In this area, the dynamic NMR measurements is an ideal technique. For example, we can take a look at the molecular motor shown in Figure 5.4. This molecular motor is composed of two rigid conjugated parts, which are not in the same plane. The rotation of the C-N bond will change the conformation of the molecule, which can be shown by the variation of the peaks of the two methyl groups in NMR spectrum. For the control of the rotation speed of this particular molecule motor, the researchers added additional functionality. When the nitrogen in the aromatic ring is not protonated the repulsion between the nitrogen and the oxygen atoms is larger which prohibits the rotation of the five member ring, which separates the peaks of the two methyl groups from each other. However, when the nitrogen is protonated, the rotation barrier greatly decreases because of the formation of a more stable coplanar transition state during the rotation process. Therefore, the speed of the rotation of the rotor dramatically increases to make the two methyl groups unrecognizable by NMR spectrometry to get an average peak. The result of the NMR spectrum versus the addition of the acid is shown in Figure 5.5, which can visually tell that the rotation speed is changing.

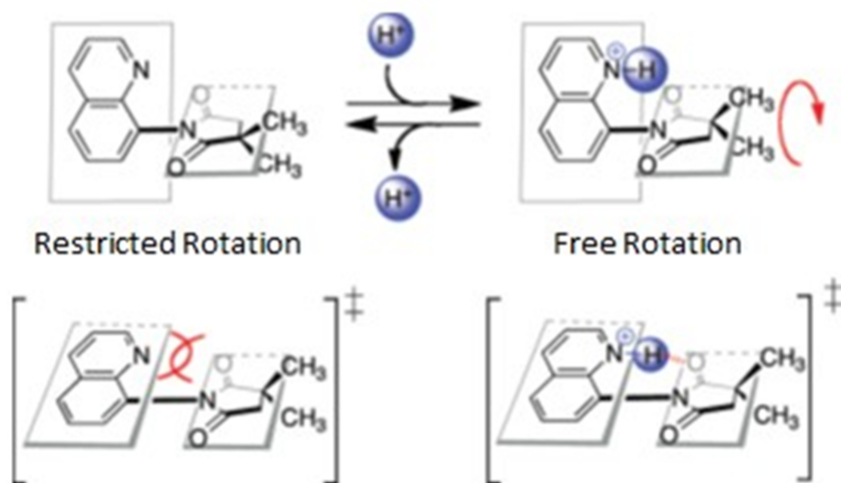


Figure 5.4: The design of molecule rotor. Reprinted with permission from B. E. Dial, P. J. Pellechia, M. D. Smith, and K. D. Shimizu, *J. Am. Chem. Soc.*, 2012, **134**, 3675. Copyright (2012) American Chemical Society.

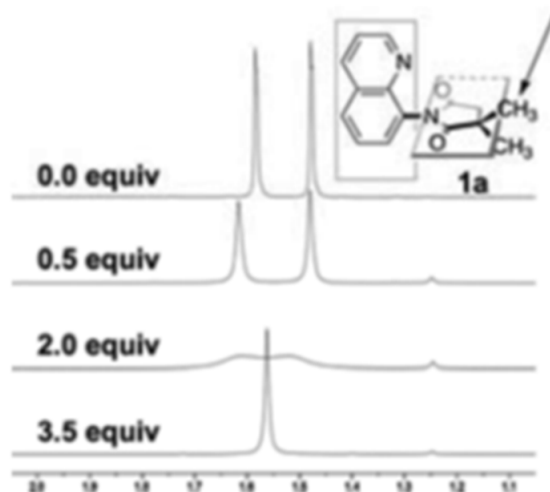


Figure 5.5: NMR spectra of the diastereotopic methyl groups of the molecular rotor with the addition of 0.0, 0.5, 2.0, and 3.5 equiv of methanesulfonic acid. Reprinted with permission from B. E. Dial, P. J. Pellechia, M. D. Smith, and K. D. Shimizu, *J. Am. Chem. Soc.*, 2012, **134**, 3675. Copyright (2012) American Chemical Society.

5.1.1 Bibliography

- J. Saad, *Dynamic NMR and Application* (2008), www.microbio.uab.edu/mic774/lectures/Saad-lecture8.pdf.
- B. E. Dial, P. J. Pellechia, M. D. Smith, and K. D. Shimizu, *J. Am. Chem. Soc.*, 2012, **134**, 3675.
- R. M. Silverstein, F. X. Webster, and D. J. Kiemle, *Spectrometric Identification of Organic Compounds*, 7th Edition, New York: Wiley, New York (2005).
- R. G. Bryant, *J. Chem. Educ.*, 1983, **60**, 933.

5.2 Rolling Molecules on Surfaces Under STM Imaging ²

5.2.1 Introduction to surface motions at the molecular level

As single molecule imaging methods such as scanning tunneling microscope (STM), atomic force microscope (AFM), and transmission electron microscope (TEM) developed in the past decades, scientists have gained powerful tools to explore molecular structures and behaviors in previously unknown areas. Among these imaging methods, STM is probably the most suitable one to observe detail at molecular level. STM can operate in a wide range of conditions, provides very high resolution, and able to manipulate molecular motions with the tip. An interesting early example came from IBM in 1990, in which the STM was used to

²This content is available online at <http://cnx.org/content/m22965/1.3/>.

position individual atoms for the first time, spelling out "IBM" in Xenon atoms. This work revealed that observation and control of single atoms and molecular motions on surfaces were possible.

The IBM work, and subsequent experiments, relied on the fact that STM tip always exerts a finite force toward an adsorbate atom that contains both van der Waals and electrostatic forces was utilized for manipulation purpose. By adjusting the position and the voltage of the tip, the interactions between the tip and the target molecule were changed. Therefore, applying/releasing force to a single atom and make it move was possible Figure 5.6.

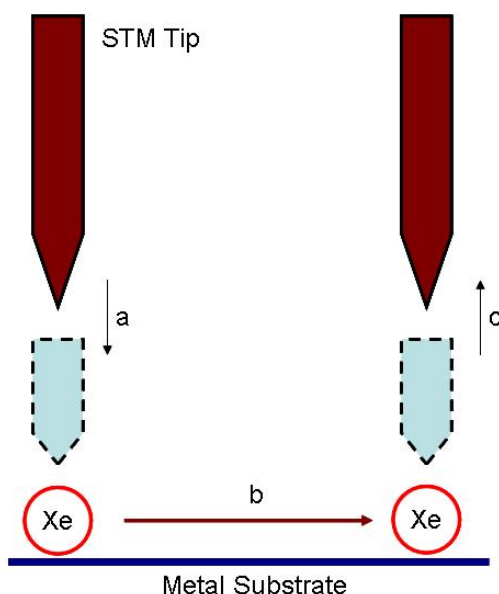


Figure 5.6: Manipulation of STM tip toward a xenon atom. a) STM tip move onto a target atom then change the voltage and current of the tip to apply a stronger interaction. b) Move the atom to a desire position. c) After reaching the desire position, the tip released by switching back to the scanning voltage and current.

The actual positioning experiment was carried out in the following process. The nickel metal substrate was prepared by cycles of argon-ion sputtering, followed by annealing in a partial pressure of oxygen to remove surface carbon and other impurities. After the cleaning process, the sample was cooled to 4 K, and imaged with the STM to ensure the quality of surface. The nickel sample was then doped with xenon. An image of the doped sample was taken at constant-current scanning conditions. Each xenon atom appears as a located randomly 1.6 Å high bump on the surface (Figure 5.7a). Under the imaging conditions (tip bias = 0.010 V with tunneling current 10^{-9} A) the interaction of the xenon with the tip is too weak to cause the position of the xenon atom to be perturbed. To move an atom, the STM tip was placed on top of the atom performing the procedure depicted in Figure 5.6 to move it to its target. Repeating this process again and again led the researcher to build of the structure they desired Figure 5.7b and c.

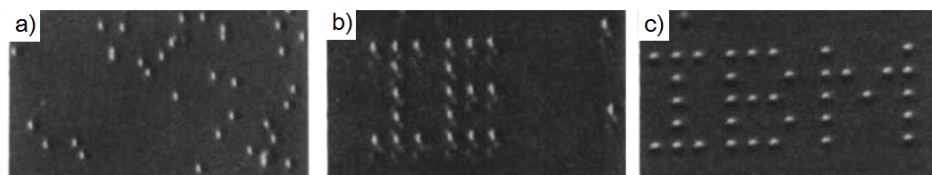


Figure 5.7: Manipulation of STM tip starting with a) randomly dosed xenon sample, b) under construction - move xenon atom to desired position, and c) accomplishment of the manipulation. Adapted from D. M. Eigler and E. K. Schweizer, *Nature*, 1990, **344**, 524.

All motions on surfaces at the single molecule level can be described as by the following (or combination of the following) modes:

- i. Sliding.
- ii. Hopping.
- iii. Rolling.
- iv. Pivoting.

Although the power of STM imaging has been demonstrated, imaging of molecules themselves is still often a difficult task. The successful imaging of the IBM work was attributed to selection of a heavy atom. Other synthetic organic molecules without heavy atoms are much more difficult to be imaged under STM. Determinations of the mechanism of molecular motion is another. Besides imaging methods themselves, other auxiliary methods such as DFT calculations and imaging of properly designed molecules are required to determine the mechanism by which a particular molecule moves across a surface.

Herein, we are particularly interested in surface-rolling molecules, i.e., those that are designed to roll on a surface. It is straightforward to imagine that if we want to construct (and image) surface-rolling molecules, we must think of making highly symmetrical structures. In addition, the magnitudes of interactions between the molecules and the surfaces have to be adequate; otherwise the molecules will be more susceptible to slide/hop or stick on the surfaces, instead of rolling. As a result, only very few molecules are known can roll and be detected on surfaces.

5.2.2 Surface rolling of molecules under the manipulation of STM tips

As described above, rolling motions are most likely to be observed on molecules having high degree of symmetry and suitable interactions between themselves and the surface. C_{60} is not only a highly symmetrical molecule but also readily imageable under STM due to its size. These properties together make C_{60} and its derivatives highly suitable to study with regards to surface-rolling motion.

The STM imaging of C_{60} was first carried out at At King College, London. Similar to the atom positioning experiment by IBM, STM tip manipulation was also utilized to achieve C_{60} displacement. The tip trajectory suggested that a rolling motion took into account the displacement on the surface of C_{60} . In order to confirm the hypothesis, the researchers also employed *ab initio* density function (DFT) calculations with rolling model boundary condition (Figure 5.8). The calculation result has supported their experimental result.

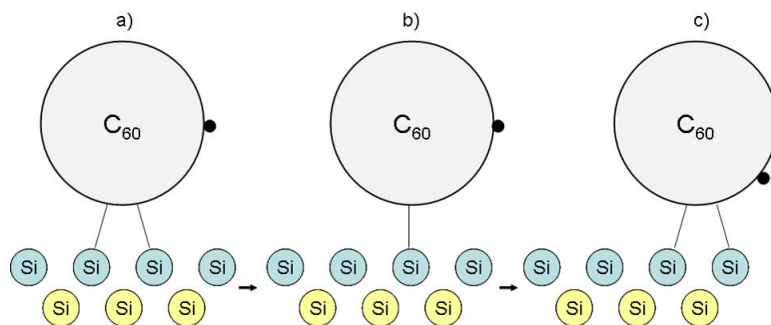


Figure 5.8: Proposed mechanism of C_{60} translation showing the alteration of C_{60} -surface interactions during rolling. a) 2-point interaction. The left point interaction was dissociated during the interaction. b) 1-point interaction. C_{60} can pivot on surface. c) 2-point interaction. A new interaction formed to complete part of the rolling motion. a) - c) The black spot on the C_{60} is moved during the manipulation. The light blue Si balls represent the first layer of molecules the silicon surface, and the yellow balls are the second layer.

The results provided insights into the dynamical response of covalently bound molecules to manipulation. The sequential breaking and reforming of highly directional covalent bonds resulted in a dynamical molecular response in which bond breaking, rotation, and translation are intimately coupled in a rolling motion (Figure 5.9), but not performing sliding or hopping motion.

A triptycene wheeled dimeric molecule Figure 5.9 was also synthesized for studying rolling motion under STM. This "tripod-like" triptycene wheel unlike a ball like C_{60} molecule also demonstrated a rolling motion on the surface. The two triptycene units were connected via a dialkynyl axle, for both desired molecule orientation sitting on surface and directional preference of the rolling motion. STM controlling and imaging was demonstrated, including the mechanism Figure 5.9.

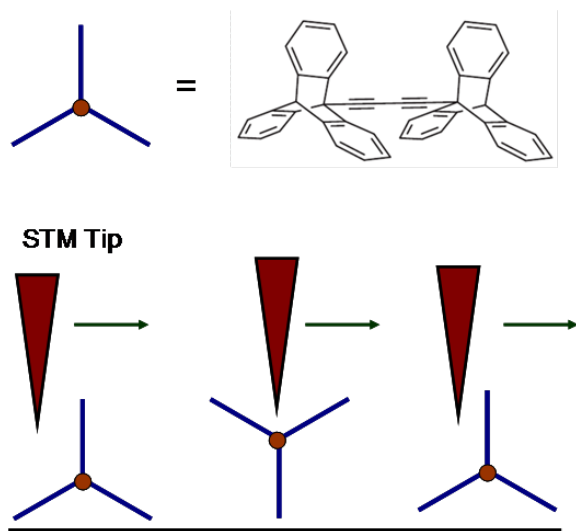


Figure 5.9: Scheme of the rolling mechanism (left to right). Step 1 is the tip approach towards the molecule, step 2 is a 120 degree rotation of a wheel around its molecular axle and in step 3 the tip reaches the other side of the molecule. It shows that, in principle, only one rotation of a wheel can be induced (the direction of movement is marked by arrows).

5.2.3 Single molecule nanocar under STM imaging

Another use of STM imaging at single molecule imaging is the single molecule nanocar by the Tour group at Rice University. The concept of a nanocar initially employed the free rotation of a C-C single bond between a spherical C_{60} molecule and an alkyne, Figure 5.10. Based on this concept, an “axle” can be designed into which are mounted C_{60} “wheels” connected with a “chassis” to construct the “nanocar”. Nanocars with this design are expected to have a directional movement perpendicular to the axle. Unfortunately, the first generation nanocar (named “nanotruck” Figure 5.11) encountered some difficulties in STM imaging due to its chemical instability and insolubility. Therefore, a new design of nanocar based on OPE has been synthesized Figure 5.12.

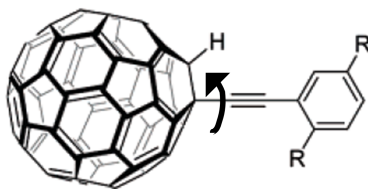


Figure 5.10: Structure of C_{60} wheels connecting to an alkyne. The only possible rolling direction is perpendicular to the C-C single bond between C_{60} and the alkyne. The arrow indicates the rotational motion of C_{60} .

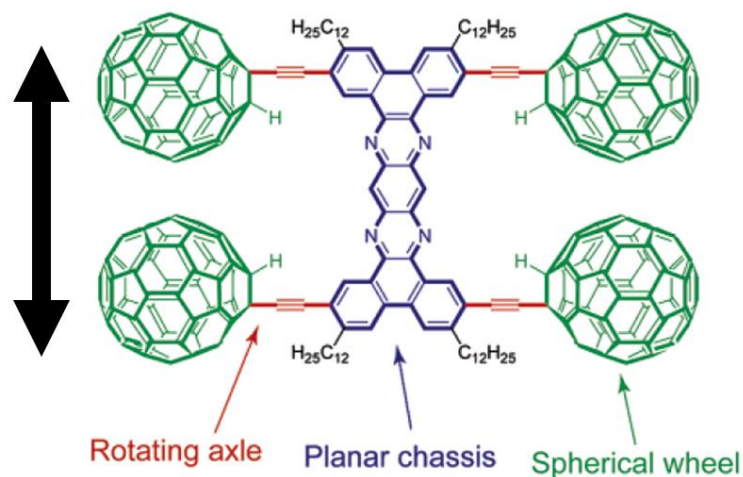


Figure 5.11: Structure of the nanotruck. No rolling motion was observed under STM imaging due to its instability, insolubility and inseparable unreacted C_{60} . The double head arrow indicates the expected direction of nanocar movement. Y. Shirai, A. J. Osgood, Y. Zhao, Y. Yao, L. Saudan, H. Yang, Y.-H. Chiu, L. B. Alemany, T. Sasaki, J.-F. Morin, J. M. Guerrero, K. F. Kelly, and J. M. Tour, *J. Am. Chem. Soc.*, 2006, **128**, 4854. Copyright American Chemical Society (2006).

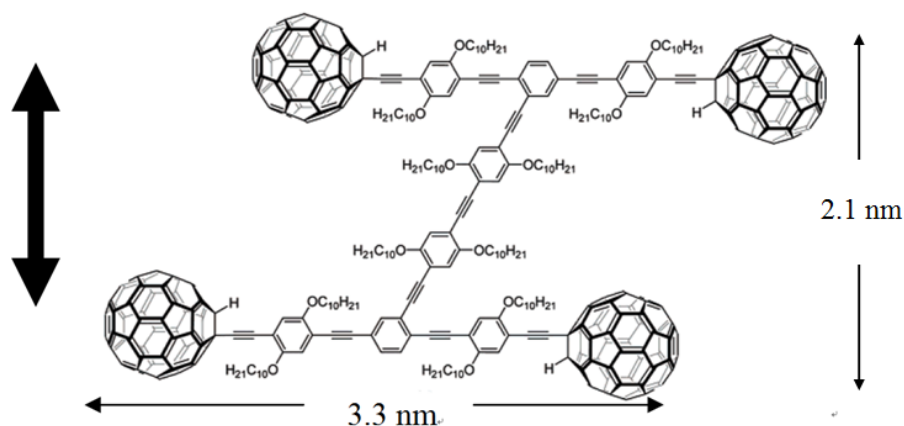


Figure 5.12: Nanocar based on OPE structure. The size of the nanocar is 3.3 nm X 2.1 nm (W x L). Alkoxy chains were attached to improve solubility and stability. OPE moiety is also separable from C₆₀. The bold double head arrow indicates the expected direction of nanocar movement. The dimension of nanocar was 3.3 nm X 2.1 nm which enable direct observation of the orientation under STM imaging. Y. Shirai, A. J. Osgood, Y. Zhao, K. F. Kelly, and J. M. Tour, *Nano Lett.*, 2005, **5**, 2330. Copyright American Chemical Society (2005).

The newly designed nanocar was studied with STM. When the nanocar was heated to ~ 200 °C, noticeable displacements of the nanocar were observed under selected images from a 10 min STM experiment Figure 5.13. The phenomenon that the nanocar moved only at high temperature was attributed their stability to a relatively strong adhesion force between the fullerene wheels and the underlying gold. The series of images showed both pivotal and translational motions on the surfaces.

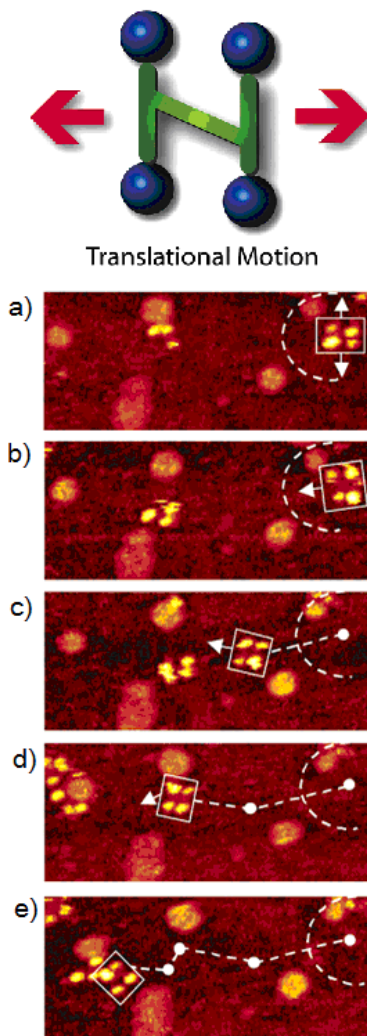


Figure 5.13: Pivotal and translational movement of OPE based nanocar. Acquisition time of one image is approximately 1 min with (a – e) images were selected from a series spanning 10 min. The configuration of the nanocar on surface can be determined by the distances of four wheels. a) – b) indicated the nanocar had made a 80° pivotal motion. b) – e) indicated translation interrupted by small-angle pivot perturbations. Y. Shirai, A. J. Osgood, Y. Zhao, K. F. Kelly, and J. M. Tour, *Nano Lett.*, 2005, **5**, 2330. Copyright American Chemical Society (2005).

Although literature studies suggested that the C_{60} molecule rolls on the surface, in the nanocar movement studies it is still not possible to conclusively conclude that the nanocar moves on surface exclusively via a rolling mechanism. Hopping, sliding and other moving modes could also be responsible for the movement of the nanocar since the experiment was carried out at high temperature conditions, making the C_{60} molecules more energetic to overcome interactions between surfaces.

To tackle the question of the mode of translation, a trimeric “nano-tricycle” has been synthesized. If the movement of fullerene-wheeled nanocar was based on a hopping or sliding mechanism, the trimer should give

observable translational motions like the four-wheeled nanocar, however, if rolling is the operable motion then the nano-tricycle should rotate on an axis, but not translate across the surface. The result of the imaging experiment of the trimer at ~ 200 °C (Figure 5.14,) yielded very small and insignificant translational displacements in comparison to 4-wheel nanocar (Figure 5.13). The trimeric 3-wheel nanocar showed some pivoting motions in the images. This motion type can be attributed to the directional preferences of the wheels mounted on the trimer causing the car to rotate. All the experimental results suggested that a C_{60} -based nanocar moves via a rolling motion rather than hopping and sliding. In addition, the fact that the thermally driven nanocar only moves in high temperature also suggests that four C_{60} have very strong interactions to the surface.

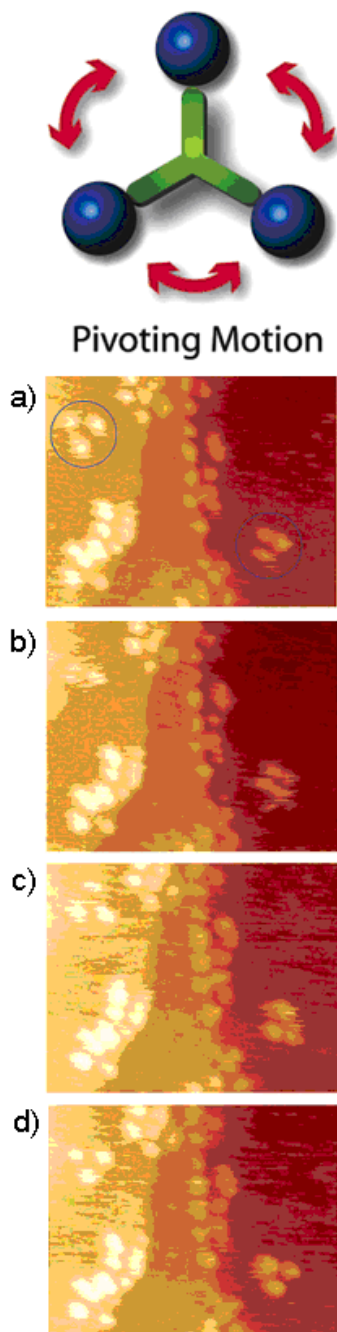


Figure 5.14: Pivot motion of the trimer. a) - d) Pivot motions of circled trimered were shown in the series of images. No significant translation were observed in comparison to the nanocar. Y. Shirai, A. J. Osgood, Y. Zhao, K. F. Kelly, and J. M. Tour, *Nano Lett.*, 2005, **5**, 2330. Copyright American Chemical Society (2005).

5.2.4 Bibliography

- D. M. Eigler and E. K. Schweizer, *Nature*, 1990, **344**, 524.
- L. Grill, K. -H. Rieder, F. Moresco, G. Rapenne, S. Stojkovic, X. Bouju, and C. Joachim, *Nat. Nanotechnol.*, 2007, **2**, 95.
- Y. Shirai, A. J. Osgood, Y. Zhao, K. F. Kelly, and J. M. Tour, *Nano Lett.*, 2005, **5**, 2330.
- Y. Shirai, A. J. Osgood, Y. Zhao, Y. Yao, L. Saudan, H. Yang, Y.-H. Chiu, L. B. Alemany, T. Sasaki, J.-F. Morin, J. M. Guerrero, K. F. Kelly, and J. M. Tour, *J. Am. Chem. Soc.*, 2006, **128**, 4854.

Chapter 6

Molecular and Solid State Structure

6.1 Crystal Structure ¹

6.1.1 Introduction

In any sort of discussion of crystalline materials, it is useful to begin with a discussion of crystallography: the study of the formation, structure, and properties of crystals. A crystal structure is defined as the particular repeating arrangement of atoms (molecules or ions) throughout a crystal. Structure refers to the internal arrangement of particles and not the external appearance of the crystal. However, these are not entirely independent since the external appearance of a crystal is often related to the internal arrangement. For example, crystals of cubic rock salt (NaCl) are physically cubic in appearance. Only a few of the possible crystal structures are of concern with respect to simple inorganic salts and these will be discussed in detail, however, it is important to understand the nomenclature of crystallography.

6.1.2 Crystallography

6.1.2.1 Bravais lattice

The Bravais lattice is the basic building block from which all crystals can be constructed. The concept originated as a topological problem of finding the number of different ways to arrange points in space where each point would have an identical “atmosphere”. That is each point would be surrounded by an identical set of points as any other point, so that all points would be indistinguishable from each other. Mathematician Auguste Bravais discovered that there were 14 different collections of the groups of points, which are known as Bravais lattices. These lattices fall into seven different “crystal systems”, as differentiated by the relationship between the angles between sides of the “unit cell” and the distance between points in the unit cell. The unit cell is the smallest group of atoms, ions or molecules that, when repeated at regular intervals in three dimensions, will produce the lattice of a crystal system. The “lattice parameter” is the length between two points on the corners of a unit cell. Each of the various lattice parameters are designated by the letters a , b , and c . If two sides are equal, such as in a tetragonal lattice, then the lengths of the two lattice parameters are designated a and c , with b omitted. The angles are designated by the Greek letters α , β , and γ , such that an angle with a specific Greek letter is not subtended by the axis with its Roman equivalent. For example, α is the included angle between the b and c axis.

Table 6.1 shows the various crystal systems, while Figure 6.1 shows the 14 Bravais lattices. It is important to distinguish the characteristics of each of the individual systems. An example of a material that takes on each of the Bravais lattices is shown in Table 6.2.

¹This content is available online at <<http://cnx.org/content/m16927/1.10/>>.

System	Axial lengths and angles	Unit cell geometry
cubic	$a = b = c, \alpha = \beta = \gamma = 90^\circ$	
tetragonal	$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$	
orthorhombic	$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$	
rhombohedral	$a = b = c, \alpha = \beta = \gamma \neq 90^\circ$	
hexagonal	$a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$	
monoclinic	$a \neq b \neq c, \alpha = \gamma = 90^\circ, \beta \neq 90^\circ$	
triclinic	$a \neq b \neq c, \alpha \neq \beta \neq \gamma$	

Table 6.1: Geometrical characteristics of the seven crystal systems.

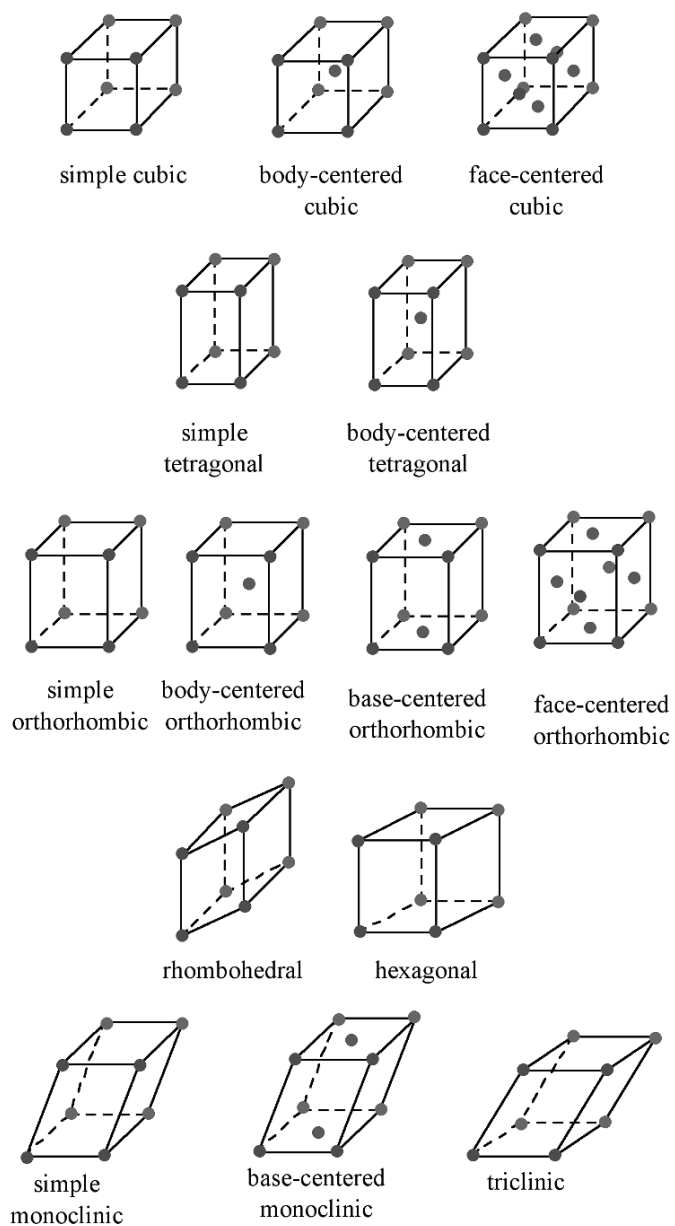


Figure 6.1: Bravais lattices.

Crystal system	Example
triclinic	$\text{K}_2\text{S}_2\text{O}_8$
monoclinic	As_4S_4 , KNO_2
rhombohedral	Hg, Sb
hexagonal	Zn, Co, NiAs
orthorhombic	Ga, Fe_3C
tetragonal	In, TiO_2
cubic	Au, Si, NaCl

Table 6.2: Examples of elements and compounds that adopt each of the crystal systems.

The cubic lattice is the most symmetrical of the systems. All the angles are equal to 90° , and all the sides are of the same length ($a = b = c$). Only the length of one of the sides (a) is required to describe this system completely. In addition to simple cubic, the cubic lattice also includes body-centered cubic and face-centered cubic (Figure 6.1). Body-centered cubic results from the presence of an atom (or ion) in the center of a cube, in addition to the atoms (ions) positioned at the vertices of the cube. In a similar manner, a face-centered cubic requires, in addition to the atoms (ions) positioned at the vertices of the cube, the presence of atoms (ions) in the center of each of the cubes face.

The tetragonal lattice has all of its angles equal to 90° , and has two out of the three sides of equal length ($a = b$). The system also includes body-centered tetragonal (Figure 6.1).

In an orthorhombic lattice all of the angles are equal to 90° , while all of its sides are of unequal length. The system needs only to be described by three lattice parameters. This system also includes body-centered orthorhombic, base-centered orthorhombic, and face-centered orthorhombic (Figure 6.1). A base-centered lattice has, in addition to the atoms (ions) positioned at the vertices of the orthorhombic lattice, atoms (ions) positioned on just two opposing faces.

The rhombohedral lattice is also known as trigonal, and has no angles equal to 90° , but all sides are of equal length ($a = b = c$), thus requiring only by one lattice parameter, and all three angles are equal ($\alpha = \beta = \gamma$).

A hexagonal crystal structure has two angles equal to 90° , with the other angle (γ) equal to 120° . For this to happen, the two sides surrounding the 120° angle must be equal ($a = b$), while the third side (c) is at 90° to the other sides and can be of any length.

The monoclinic lattice has no sides of equal length, but two of the angles are equal to 90° , with the other angle (usually defined as β) being something other than 90° . It is a tilted parallelogram prism with rectangular bases. This system also includes base-centered monoclinic (Figure 6.1).

In the triclinic lattice none of the sides of the unit cell are equal, and none of the angles within the unit cell are equal to 90° . The triclinic lattice is chosen such that all the internal angles are either acute or obtuse. This crystal system has the lowest symmetry and must be described by 3 lattice parameters (a , b , and c) and the 3 angles (α , β , and γ).

6.1.2.2 Atom positions, crystal directions and Miller indices

6.1.2.2.1 Atom positions and crystal axes

The structure of a crystal is defined with respect to a unit cell. As the entire crystal consists of repeating unit cells, this definition is sufficient to represent the entire crystal. Within the unit cell, the atomic arrangement is expressed using coordinates. There are two systems of coordinates commonly in use, which can cause some confusion. Both use a corner of the unit cell as their origin. The first, less-commonly seen system is that of Cartesian or orthogonal coordinates (X , Y , Z). These usually have the units of Angstroms and relate to the distance in each direction between the origin of the cell and the atom. These coordinates may be

manipulated in the same fashion are used with two- or three-dimensional graphs. It is very simple, therefore, to calculate inter-atomic distances and angles given the Cartesian coordinates of the atoms. Unfortunately, the repeating nature of a crystal cannot be expressed easily using such coordinates. For example, consider a cubic cell of dimension 3.52 Å. Pretend that this cell contains an atom that has the coordinates (1.5, 2.1, 2.4). That is, the atom is 1.5 Å away from the origin in the *x* direction (which coincides with the *a* cell axis), 2.1 Å in the *y* (which coincides with the *b* cell axis) and 2.4 Å in the *z* (which coincides with the *c* cell axis). There will be an equivalent atom in the next unit cell along the *x*-direction, which will have the coordinates (1.5 + 3.52, 2.1, 2.4) or (5.02, 2.1, 2.4). This was a rather simple calculation, as the cell has very high symmetry and so the cell axes, *a*, *b* and *c*, coincide with the Cartesian axes, *X*, *Y* and *Z*. However, consider lower symmetry cells such as triclinic or monoclinic in which the cell axes are not mutually orthogonal. In such cases, expressing the repeating nature of the crystal is much more difficult to accomplish.

Accordingly, atomic coordinates are usually expressed in terms of fractional coordinates, (*x*, *y*, *z*). This coordinate system is coincident with the cell axes (*a*, *b*, *c*) and relates to the position of the atom in terms of the fraction along each axis. Consider the atom in the cubic cell discussion above. The atom was 1.5 Å in the *a* direction away from the origin. As the *a* axis is 3.52 Å long, the atom is $(1.5/3.52)$ or 0.43 of the axis away from the origin. Similarly, it is $(2.1/3.52)$ or 0.60 of the *b* axis and $(2.4/3.52)$ or 0.68 of the *c* axis. The fractional coordinates of this atom are, therefore, (0.43, 0.60, 0.68). The coordinates of the equivalent atom in the next cell over in the *a* direction, however, are easily calculated as this atom is simply 1 unit cell away in *a*. Thus, all one has to do is add 1 to the *x* coordinate: (1.43, 0.60, 0.68). Such transformations can be performed regardless of the shape of the unit cell. Fractional coordinates, therefore, are used to retain and manipulate crystal information.

6.1.2.2.2 Crystal directions

The designation of the individual vectors within any given crystal lattice is accomplished by the use of whole number multipliers of the lattice parameter of the point at which the vector exits the unit cell. The vector is indicated by the notation $[hkl]$, where *h*, *k*, and *l* are reciprocals of the point at which the vector exits the unit cell. The origination of all vectors is assumed defined as $[000]$. For example, the direction along the *a*-axis according to this scheme would be $[100]$ because this has a component only in the *a*-direction and no component along either the *b* or *c* axial direction. A vector diagonally along the face defined by the *a* and *b* axis would be $[110]$, while going from one corner of the unit cell to the opposite corner would be in the $[111]$ direction. Figure 6.2 shows some examples of the various directions in the unit cell. The crystal direction notation is made up of the lowest combination of integers and represents unit distances rather than actual distances. A $[222]$ direction is identical to a $[111]$, so $[111]$ is used. Fractions are not used. For example, a vector that intercepts the center of the top face of the unit cell has the coordinates *x* = 1/2, *y* = 1/2, *z* = 1. All have to be inversed to convert to the lowest combination of integers (whole numbers); i.e., $[221]$ in Figure 6.2. Finally, all parallel vectors have the same crystal direction, e.g., the four vertical edges of the cell shown in Figure 6.2 all have the crystal direction $[hkl] = [001]$.

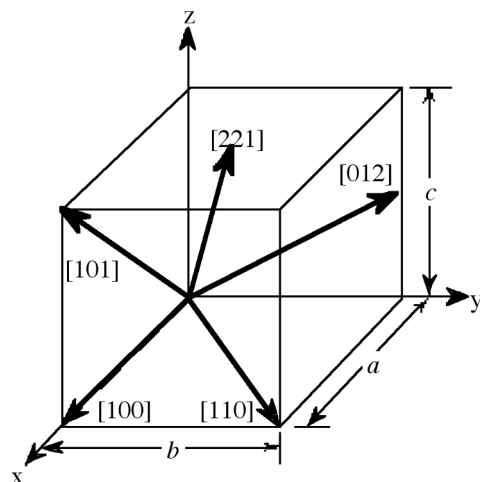


Figure 6.2: Some common directions in a cubic unit cell.

Crystal directions may be grouped in families. To avoid confusion there exists a convention in the choice of brackets surrounding the three numbers to differentiate a crystal direction from a family of direction. For a direction, square brackets $[hkl]$ are used to indicate an individual direction. Angle brackets $\langle hkl \rangle$ indicate a family of directions. A family of directions includes any directions that are equivalent in length and types of atoms encountered. For example, in a cubic lattice, the $[100]$, $[010]$, and $[001]$ directions all belong to the $\langle 100 \rangle$ family of planes because they are equivalent. If the cubic lattice were rotated 90° , the a , b , and c directions would remain indistinguishable, and there would be no way of telling on which crystallographic positions the atoms are situated, so the family of directions is the same. In a hexagonal crystal, however, this is not the case, so the $[100]$ and $[010]$ would both be $\langle 100 \rangle$ directions, but the $[001]$ direction would be distinct. Finally, negative directions are identified with a bar over the negative number instead of a minus sign.

6.1.2.2.3 Crystal planes

Planes in a crystal can be specified using a notation called Miller indices. The Miller index is indicated by the notation $[hkl]$ where h , k , and l are reciprocals of the plane with the x , y , and z axes. To obtain the Miller indices of a given plane requires the following steps:

- Step 1. The plane in question is placed on a unit cell.
- Step 2. Its intercepts with each of the crystal axes are then found.
- Step 3. The reciprocal of the intercepts are taken.
- Step 4. These are multiplied by a scalar to insure that is in the simple ratio of whole numbers.

For example, the face of a lattice that does not intersect the y or z axis would be (100) , while a plane along the body diagonal would be the (111) plane. An illustration of this along with the (111) and (110) planes is given in Figure 6.3.

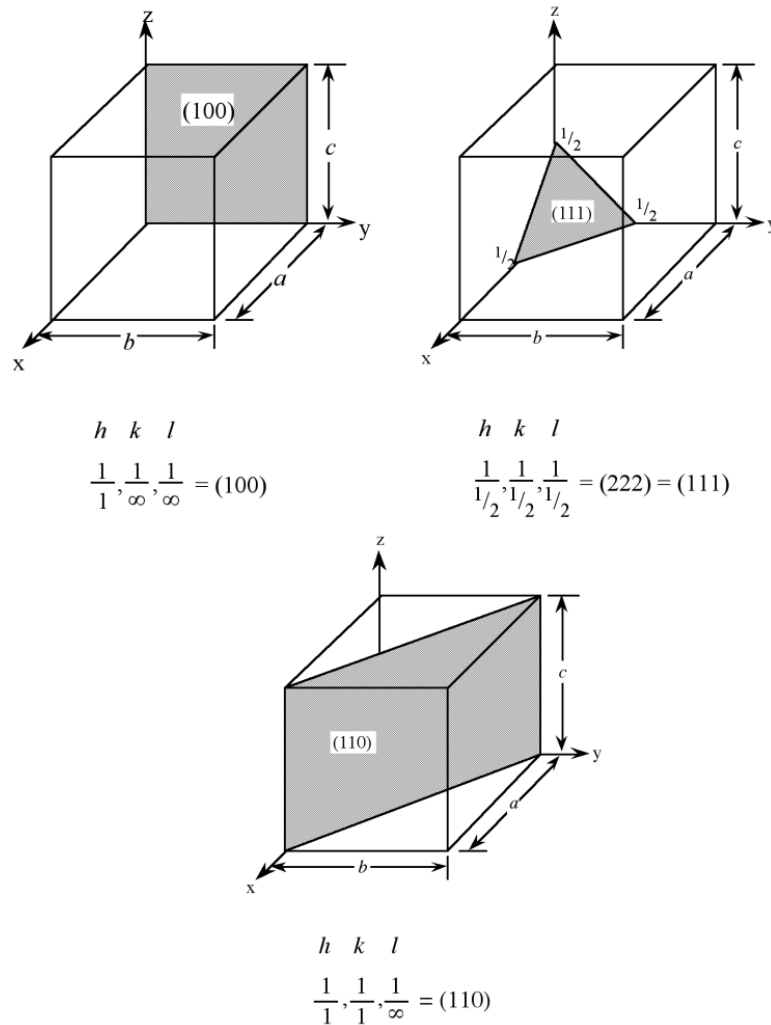


Figure 6.3: Examples of Miller indices notation for crystal planes.

As with crystal directions, Miller indices directions may be grouped in families. Individual Miller indices are given in parentheses (hkl), while braces $\{hkl\}$ are placed around the indices of a family of planes. For example, (001), (100), and (010) are all in the $\{100\}$ family of planes, for a cubic lattice.

6.1.3 Description of crystal structures

Crystal structures may be described in a number of ways. The most common manner is to refer to the size and shape of the unit cell and the positions of the atoms (or ions) within the cell. However, this information is sometimes insufficient to allow for an understanding of the true structure in three dimensions. Consideration of several unit cells, the arrangement of the atoms with respect to each other, the number of other atoms they in contact with, and the distances to neighboring atoms, often will provide a better understanding. A number of methods are available to describe extended solid-state structures. The most applicable with

regard to elemental and compound semiconductor, metals and the majority of insulators is the close packing approach.

6.1.3.1 Close packed structures: hexagonal close packing and cubic close packing

Many crystal structures can be described using the concept of close packing. This concept requires that the atoms (ions) are arranged so as to have the maximum density. In order to understand close packing in three dimensions, the most efficient way for equal sized spheres to be packed in two dimensions must be considered.

The most efficient way for equal sized spheres to be packed in two dimensions is shown in Figure 6.4, in which it can be seen that each sphere (the dark gray shaded sphere) is surrounded by, and is in contact with, six other spheres (the light gray spheres in Figure 6.4). It should be noted that contact with six other spheres the maximum possible is the spheres are the same size, although lower density packing is possible. Close packed layers are formed by repetition to an infinite sheet. Within these close packed layers, three close packed rows are present, shown by the dashed lines in Figure 6.4.

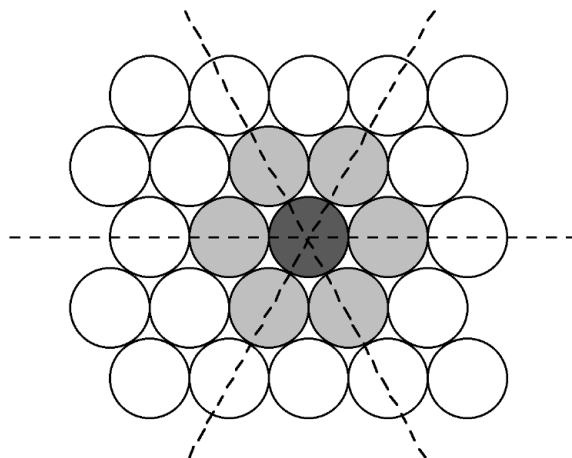


Figure 6.4: Schematic representation of a close packed layer of equal sized spheres. The close packed rows (directions) are shown by the dashed lines.

The most efficient way for equal sized spheres to be packed in three dimensions is to stack close packed layers on top of each other to give a close packed structure. There are two simple ways in which this can be done, resulting in either a hexagonal or cubic close packed structures.

6.1.3.1.1 Hexagonal close packed

If two close packed layers A and B are placed in contact with each other so as to maximize the density, then the spheres of layer B will rest in the hollow (vacancy) between three of the spheres in layer A. This is demonstrated in Figure 6.5. Atoms in the second layer, B (shaded light gray), may occupy one of two possible positions (Figure 6.5a or b) but not both together or a mixture of each. If a third layer is placed on top of layer B such that it exactly covers layer A, subsequent placement of layers will result in the following sequence ...ABABAB.... This is known as hexagonal close packing or *hcp*.

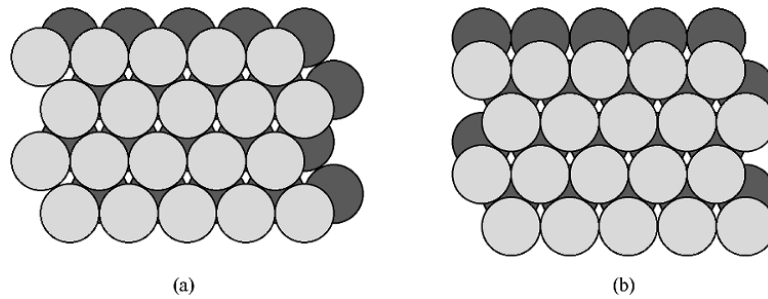


Figure 6.5: Schematic representation of two close packed layers arranged in A (dark grey) and B (light grey) positions. The alternative stacking of the B layer is shown in (a) and (b).

The hexagonal close packed cell is a derivative of the hexagonal Bravais lattice system (Figure 6.1) with the addition of an atom inside the unit cell at the coordinates $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$. The basal plane of the unit cell coincides with the close packed layers (Figure 6.6). In other words the close packed layer makes-up the $\{001\}$ family of crystal planes.

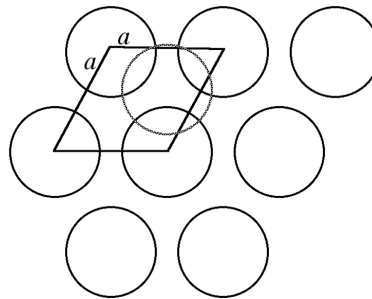


Figure 6.6: A schematic projection of the basal plane of the hcp unit cell on the close packed layers.

The “packing fraction” in a hexagonal close packed cell is 74.05%; that is 74.05% of the total volume is occupied. The packing fraction or density is derived by assuming that each atom is a hard sphere in contact with its nearest neighbors. Determination of the packing fraction is accomplished by calculating the number of whole spheres per unit cell (2 in hcp), the volume occupied by these spheres, and a comparison with the total volume of a unit cell. The number gives an idea of how “open” or filled a structure is. By comparison, the packing fraction for body-centered cubic (Figure 6.1) is 68% and for diamond cubic (an important semiconductor structure to be described later) is 34%.

6.1.3.1.2 Cubic close packed: face-centered cubic

In a similar manner to the generation of the hexagonal close packed structure, two close packed layers are stacked (Figure 6.4) however, the third layer (C) is placed such that it does not exactly cover layer A,

while sitting in a set of troughs in layer B (Figure 6.7), then upon repetition the packing sequence will be ...ABCABCABC.... This is known as cubic close packing or *ccp*.

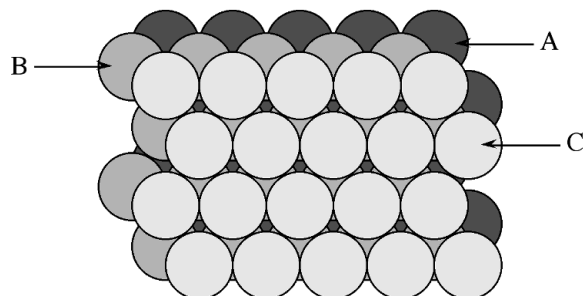


Figure 6.7: Schematic representation of the three close packed layers in a cubic close packed arrangement: A (dark grey), B (medium grey), and C (light grey).

The unit cell of cubic close packed structure is actually that of a face-centered cubic (*fcc*) Bravais lattice. In the *fcc* lattice the close packed layers constitute the $\{111\}$ planes. As with the *hcp* lattice packing fraction in a cubic close packed (*fcc*) cell is 74.05%. Since face centered cubic or *fcc* is more commonly used in preference to cubic close packed (*ccp*) in describing the structures, the former will be used throughout this text.

6.1.3.2 Coordination number

The coordination number of an atom or ion within an extended structure is defined as the number of nearest neighbor atoms (ions of opposite charge) that are in contact with it. A slightly different definition is often used for atoms within individual molecules: the number of donor atoms associated with the central atom or ion. However, this distinction is rather artificial, and both can be employed.

The coordination numbers for metal atoms in a molecule or complex are commonly 4, 5, and 6, but all values from 2 to 9 are known and a few examples of higher coordination numbers have been reported. In contrast, common coordination numbers in the solid state are 3, 4, 6, 8, and 12. For example, the atom in the center of body-centered cubic lattice has a coordination number of 8, because it touches the eight atoms at the corners of the unit cell, while an atom in a simple cubic structure would have a coordination number of 6. In both *fcc* and *hcp* lattices each of the atoms have a coordination number of 12.

6.1.3.3 Octahedral and tetrahedral vacancies

As was mentioned above, the packing fraction in both *fcc* and *hcp* cells is 74.05%, leaving 25.95% of the volume unfilled. The unfilled lattice sites (interstices) between the atoms in a cell are called interstitial sites or vacancies. The shape and relative size of these sites is important in controlling the position of additional atoms. In both *fcc* and *hcp* cells most of the space within these atoms lies within two different sites known as octahedral sites and tetrahedral sites. The difference between the two lies in their “coordination number”, or the number of atoms surrounding each site. Tetrahedral sites (vacancies) are surrounded by four atoms arranged at the corners of a tetrahedron. Similarly, octahedral sites are surrounded by six atoms which make-up the apices of an octahedron. For a given close packed lattice an octahedral vacancy will be larger than a tetrahedral vacancy.

Within a face centered cubic lattice, the eight tetrahedral sites are positioned within the cell, at the general fractional coordinate of $(n/4, n/4, n/4)$ where $n = 1$ or 3 , e.g., $(1/4, 1/4, 1/4)$, $(1/4, 1/4, 3/4)$, etc. The

octahedral sites are located at the center of the unit cell ($1/2, 1/2, 1/2$), as well as at each of the edges of the cell, e.g., ($1/2, 0, 0$). In the hexagonal close packed system, the tetrahedral sites are at ($0, 0, 3/8$) and ($1/3, 2/3, 7/8$), and the octahedral sites are at ($1/3, 1/3, 1/4$) and all symmetry equivalent positions.

6.1.3.4 Important structure types

The majority of crystalline materials do not have a structure that fits into the one atom per site simple Bravais lattice. A number of other important crystal structures are found, however, only a few of these crystal structures are those of which occur for the elemental and compound semiconductors and the majority of these are derived from *fcc* or *hcp* lattices. Each structural type is generally defined by an archetype, a material (often a naturally occurring mineral) which has the structure in question and to which all the similar materials are related. With regard to commonly used elemental and compound semiconductors the important structures are diamond, zinc blende, Wurtzite, and to a lesser extent chalcopyrite. However, rock salt, β -tin, cinnabar and cesium chloride are observed as high pressure or high temperature phases and are therefore also discussed. The following provides a summary of these structures. Details of the full range of solid-state structures are given elsewhere.

6.1.3.4.1 Diamond Cubic

The diamond cubic structure consists of two interpenetrating face-centered cubic lattices, with one offset $1/4$ of a cube along the cube diagonal. It may also be described as face centered cubic lattice in which half of the tetrahedral sites are filled while all the octahedral sites remain vacant. The diamond cubic unit cell is shown in Figure 6.8. Each of the atoms (e.g., C) is four coordinate, and the shortest interatomic distance (C-C) may be determined from the unit cell parameter (a).

$$\text{C-C} = \frac{a\sqrt{3}}{4} \approx 0.422 a \quad (6.1)$$

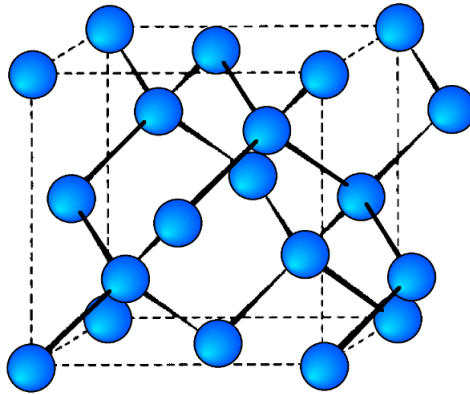


Figure 6.8: Unit cell structure of a diamond cubic lattice showing the two interpenetrating face-centered cubic lattices.

6.1.3.4.2 Zinc blende

This is a binary phase (ME) and is named after its archetype, a common mineral form of zinc sulfide (ZnS). As with the diamond lattice, zinc blende consists of the two interpenetrating *fcc* lattices. However, in zinc blende one lattice consists of one of the types of atoms (Zn in ZnS), and the other lattice is of the second type of atom (S in ZnS). It may also be described as face centered cubic lattice of S atoms in which half of the tetrahedral sites are filled with Zn atoms. All the atoms in a zinc blende structure are 4-coordinate. The zinc blende unit cell is shown in Figure 6.9. A number of inter-atomic distances may be calculated for any material with a zinc blende unit cell using the lattice parameter (a).

$$\text{Zn-S} = a \frac{\sqrt{3}}{4} \approx 0.422 a \quad (6.2)$$

$$\text{Zn-Zn} = \text{S-S} = \frac{a}{\sqrt{2}} \approx 0.707 a \quad (6.3)$$

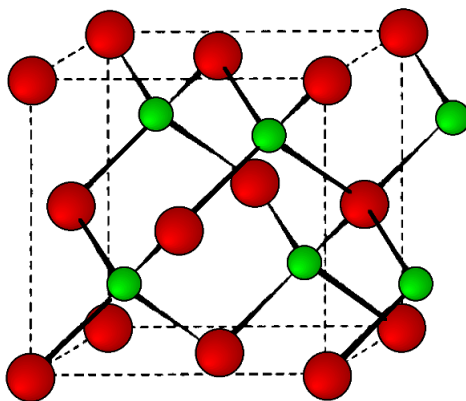


Figure 6.9: Unit cell structure of a zinc blende (ZnS) lattice. Zinc atoms are shown in green (small), sulfur atoms shown in red (large), and the dashed lines show the unit cell.

6.1.3.4.3 Chalcopyrite

The mineral chalcopyrite CuFeS_2 is the archetype of this structure. The structure is tetragonal ($a = b \neq c$, $\alpha = \beta = \gamma = 90^\circ$), and is essentially a superlattice on that of zinc blende. Thus, is easiest to imagine that the chalcopyrite lattice is made-up of a lattice of sulfur atoms in which the tetrahedral sites are filled in layers, ...FeCuCuFe..., etc. (Figure 6.10). In such an idealized structure $c = 2a$, however, this is not true of all materials with chalcopyrite structures.

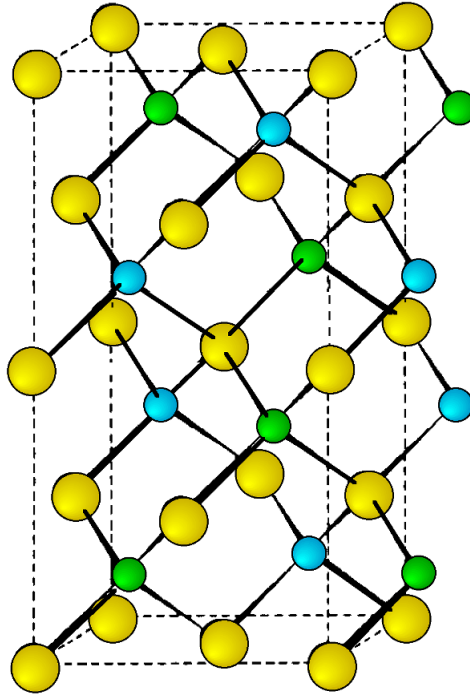


Figure 6.10: Unit cell structure of a chalcopyrite lattice. Copper atoms are shown in blue, iron atoms are shown in green and sulfur atoms are shown in yellow. The dashed lines show the unit cell.

6.1.3.4.4 Rock salt

As its name implies the archetypal rock salt structure is NaCl (table salt). In common with the zinc blende structure, rock salt consists of two interpenetrating face-centered cubic lattices. However, the second lattice is offset $1/2a$ along the unit cell axis. It may also be described as face centered cubic lattice in which all of the octahedral sites are filled, while all the tetrahedral sites remain vacant, and thus each of the atoms in the rock salt structure are 6-coordinate. The rock salt unit cell is shown in Figure 6.11. A number of inter-atomic distances may be calculated for any material with a rock salt structure using the lattice parameter (a).

$$\text{Na-Cl} = \frac{a}{2} \approx 0.5 a \quad (6.4)$$

$$\text{Na-Na} = \text{Cl-Cl} = \frac{a}{\sqrt{2}} \approx 0.707 a \quad (6.5)$$

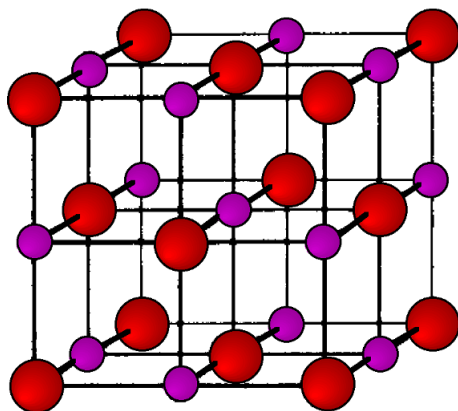


Figure 6.11: Unit cell structure of a rock salt lattice. Sodium ions are shown in purple (small spheres) and chloride ions are shown in red (large spheres).

6.1.3.4.5 Cinnabar

Cinnabar, named after the archetype mercury sulfide, HgS , is a distorted rock salt structure in which the resulting cell is rhombohedral (trigonal) with each atom having a coordination number of six.

6.1.3.4.6 Wurtzite

This is a hexagonal form of the zinc sulfide. It is identical in the number of and types of atoms, but it is built from two interpenetrating *hcp* lattices as opposed to the *fcc* lattices in zinc blende. As with zinc blende all the atoms in a wurtzite structure are 4-coordinate. The wurtzite unit cell is shown in Figure 6.12. A number of inter atomic distances may be calculated for any material with a wurtzite cell using the lattice parameter (a).

$$\text{Zn-S} = a\sqrt{3}/8 = 0.612a = \frac{3c}{8} = 0.375c \quad (6.6)$$

$$\text{Zn-Zn} = \text{S-S} = a = 1.632c \quad (6.7)$$

However, it should be noted that these formulae do not necessarily apply when the ratio a/c is different from the ideal value of 1.632.

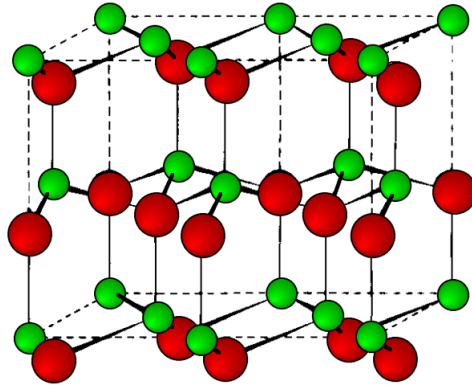


Figure 6.12: Unit cell structure of a wurtzite lattice. Zinc atoms are shown in green (small spheres), sulfur atoms shown in red (large spheres), and the dashed lines show the unit cell.

6.1.3.4.7 Cesium Chloride

The cesium chloride structure is found in materials with large cations and relatively small anions. It has a simple (primitive) cubic cell (Figure 6.1) with a chloride ion at the corners of the cube and the cesium ion at the body center. The coordination numbers of both Cs^+ and Cl^- , with the inner atomic distances determined from the cell lattice constant (a).

$$\text{Cs-Cl} = \frac{a\sqrt{3}}{2} \approx 0.866 a \quad (6.8)$$

$$\text{Cs-Cs} = \text{Cl-Cl} = a \quad (6.9)$$

6.1.3.4.8 β -Tin.

The room temperature allotrope of tin is β -tin or white tin. It has a tetragonal structure, in which each tin atom has four nearest neighbors ($\text{Sn-Sn} = 3.016 \text{ \AA}$) arranged in a very flattened tetrahedron, and two next nearest neighbors ($\text{Sn-Sn} = 3.175 \text{ \AA}$). The overall structure of β -tin consists of fused hexagons, each being linked to its neighbor via a four-membered Sn_4 ring.

6.1.4 Defects in crystalline solids

Up to this point we have only been concerned with ideal structures for crystalline solids in which each atom occupies a designated point in the crystal lattice. Unfortunately, defects ordinarily exist in equilibrium between the crystal lattice and its environment. These defects are of two general types: point defects and extended defects. As their names imply, point defects are associated with a single crystal lattice site, while extended defects occur over a greater range.

6.1.4.1 Point defects: “too many or too few” or “just plain wrong”

Point defects have a significant effect on the properties of a semiconductor, so it is important to understand the classes of point defects and the characteristics of each type. Figure 6.13 summarizes various classes of native point defects, however, they may be divided into two general classes; defects with the wrong number of atoms (deficiency or surplus) and defects where the identity of the atoms is incorrect.

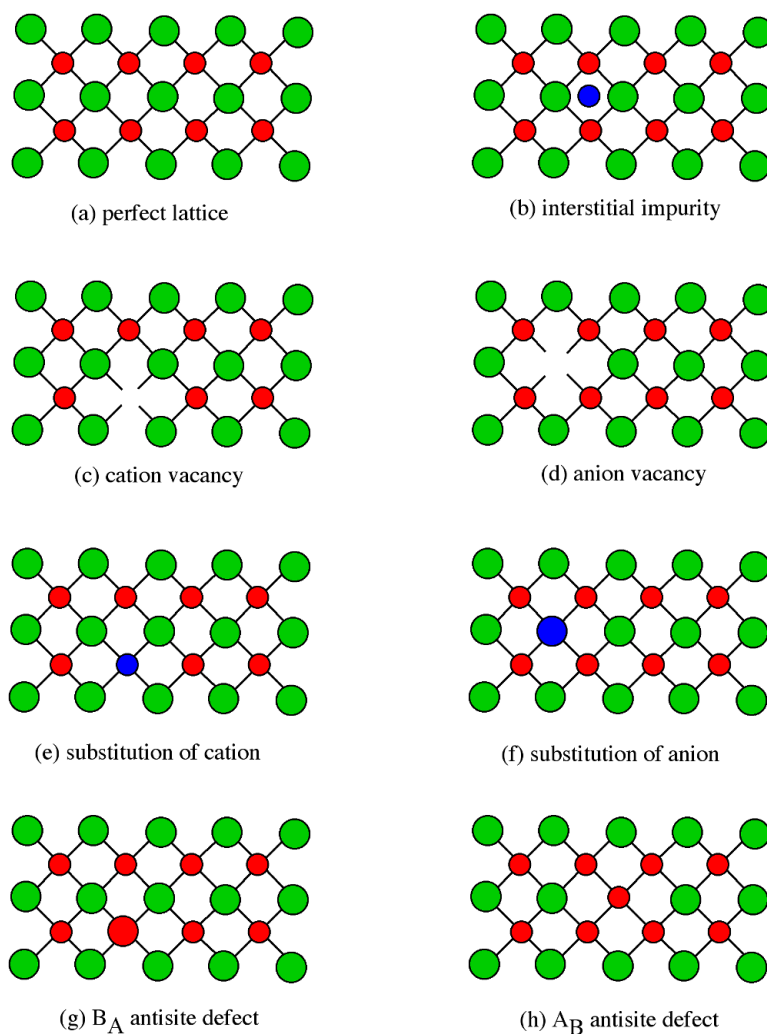


Figure 6.13: Point defects in a crystal lattice.

6.1.4.1.1 Interstitial Impurity

An interstitial impurity occurs when an extra atom is positioned in a lattice site that should be vacant in an ideal structure (Figure 6.13b). Since all the adjacent lattice sites are filled the additional atom will have to squeeze itself into the interstitial site, resulting in distortion of the lattice and alteration in the local

electronic behavior of the structure. Small atoms, such as carbon, will prefer to occupy these interstitial sites. Interstitial impurities readily diffuse through the lattice via interstitial diffusion, which can result in a change of the properties of a material as a function of time. Oxygen impurities in silicon generally are located as interstitials.

6.1.4.1.2 Vacancies

The converse of an interstitial impurity is when there are not enough atoms in a particular area of the lattice. These are called vacancies. Vacancies exist in any material above absolute zero and increase in concentration with temperature. In the case of compound semiconductors, vacancies can be either cation vacancies (Figure 6.13c) or anion vacancies (Figure 6.13d), depending on what type of atom are “missing”.

6.1.4.1.3 Substitution

Substitution of various atoms into the normal lattice structure is common, and used to change the electronic properties of both compound and elemental semiconductors. Any impurity element that is incorporated during crystal growth can occupy a lattice site. Depending on the impurity, substitution defects can greatly distort the lattice and/or alter the electronic structure. In general, cations will try to occupy cation lattice sites (Figure 6.13e), and anion will occupy the anion site (Figure 6.13f). For example, a zinc impurity in GaAs will occupy a gallium site, if possible, while a sulfur, selenium and tellurium atoms would all try to substitute for an arsenic. Some impurities will occupy either site indiscriminately, e.g., Si and Sn occupy both Ga and As sites in GaAs.

6.1.4.1.4 Antisite Defects

Antisite defects are a particular form of substitution defect, and are unique to compound semiconductors. An antisite defect occurs when a cation is misplaced on an anion lattice site or vice versa (Figure 6.13g and h). Depending on the arrangement these are designated as either A_B antisite defects or B_A antisite defects. For example, if an arsenic atom is on a gallium lattice site the defect would be an As_{Ga} defect. Antisite defects involve fitting into a lattice site atoms of a different size than the rest of the lattice, and therefore this often results in a localized distortion of the lattice. In addition, cations and anions will have a different number of electrons in their valence shells, so this substitution will alter the local electron concentration and the electronic properties of this area of the semiconductor.

6.1.4.2 Extended Defects: Dislocations in a Crystal Lattice

Extended defects may be created either during crystal growth or as a consequence of stress in the crystal lattice. The plastic deformation of crystalline solids does not occur such that all bonds along a plane are broken and reformed simultaneously. Instead, the deformation occurs through a dislocation in the crystal lattice. Figure 6.14 shows a schematic representation of a dislocation in a crystal lattice. Two features of this type of dislocation are the presence of an extra crystal plane, and a large void at the dislocation core. Impurities tend to segregate to the dislocation core in order to relieve strain from their presence.

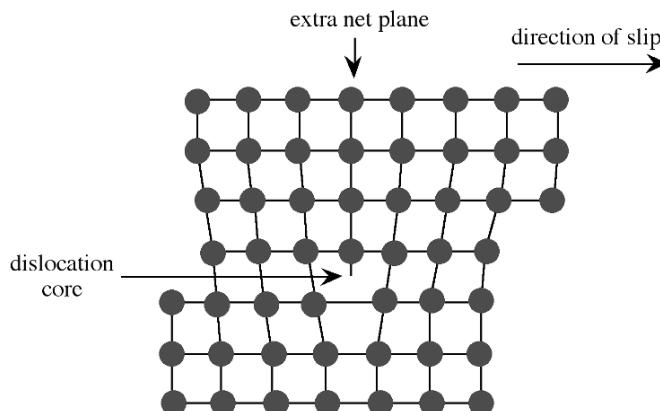


Figure 6.14: Dislocation in a crystal lattice.

6.1.5 Epitaxy

Epitaxy, is a transliteration of two Greek words *epi*, meaning "upon", and *taxis*, meaning "ordered". With respect to crystal growth it applies to the process of growing thin crystalline layers on a crystal substrate. In epitaxial growth, there is a precise crystal orientation of the film in relation to the substrate. The growth of epitaxial films can be done by a number of methods including molecular beam epitaxy, atomic layer epitaxy, and chemical vapor deposition, all of which will be described later.

Epitaxy of the same material, such as a gallium arsenide film on a gallium arsenide substrate, is called homoepitaxy, while epitaxy where the film and substrate material are different is called heteroepitaxy. Clearly, in homoepitaxy, the substrate and film will have the identical structure, however, in heteroepitaxy, it is important to employ where possible a substrate with the same structure and similar lattice parameters. For example, zinc selenide (zinc blende, $a = 5.668 \text{ \AA}$) is readily grown on gallium arsenide (zinc blende, $a = 5.653 \text{ \AA}$). Alternatively, epitaxial crystal growth can occur where there exists a simple relationship between the structures of the substrate and crystal layer, such as is observed between Al_2O_3 (100) on Si (100). Whichever route is chosen a close match in the lattice parameters is required, otherwise, the strains induced by the lattice mismatch results in distortion of the film and formation of dislocations. If the mismatch is significant epitaxial growth is not energetically favorable, causing a textured film or polycrystalline untextured film to be grown. As a general rule of thumb, epitaxy can be achieved if the lattice parameters of the two materials are within about 5% of each other. For good quality epitaxy, this should be less than 1%. The larger the mismatch, the larger the strain in the film. As the film gets thicker and thicker, it will try to relieve the strain in the film, which could include the loss of epitaxy or the growth of dislocations. It is important to note that the $\langle 100 \rangle$ directions of a film must be parallel to the $\langle 100 \rangle$ direction of the substrate. In some cases, such as Fe on MgO, the $[111]$ direction is parallel to the substrate $[100]$. The epitaxial relationship is specified by giving first the plane in the film that is parallel to the substrate $[100]$.

6.1.6 Bibliography

- *International Tables for X-ray Crystallography*. Vol. IV; Kynoch Press: Birmingham, UK (1974).
- B. F. G. Johnson, in *Comprehensive Inorganic Chemistry*, Pergamon Press, Vol. 4, Chapter 52 (1973).
- A. R. West, *Solid State Chemistry and its Applications*, Wiley, New York (1984).

6.2 Structures of Element and Compound Semiconductors ²

6.2.1 Introduction

A single crystal of either an elemental (e.g., silicon) or compound (e.g., gallium arsenide) semiconductor forms the basis of almost all semiconductor devices. The ability to control the electronic and opto-electronic properties of these materials is based on an understanding of their structure. In addition, the metals and many of the insulators employed within a microelectronic device are also crystalline.

6.2.2 Group IV (14) elements

Each of the semiconducting phases of the group IV (14) elements, C (diamond), Si, Ge, and α -Sn, adopt the diamond cubic structure (Figure 6.15). Their lattice constants (a , Å) and densities (ρ , g/cm³) are given in Table 6.3.

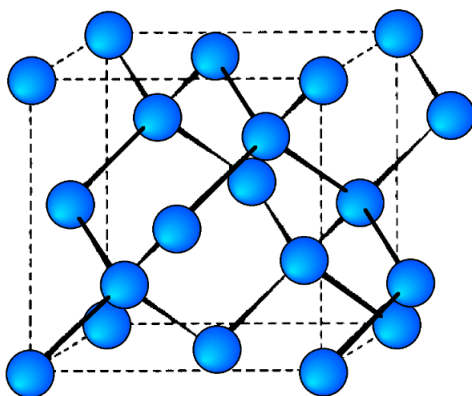


Figure 6.15: Unit cell structure of a diamond cubic lattice showing the two interpenetrating face-centered cubic lattices.

Element	Lattice parameter, a (Å)	Density (g/cm ³)
carbon (diamond)	3.56683(1)	3.51525
silicon	5.4310201(3)	2.319002
germanium	5.657906(1)	5.3234
tin (α -Sn)	6.4892(1)	7.285

Table 6.3: Lattice parameters and densities (measured at 298 K) for the diamond cubic forms of the group IV (14) elements.

As would be expected the lattice parameter increase in the order $C < Si < Ge < \alpha\text{-Sn}$. Silicon and germanium form a continuous series of solid solutions with gradually varying parameters. It is worth noting the high degree of accuracy that the lattice parameters are known for high purity crystals of these elements. In addition, it is important to note the temperature at which structural measurements are made, since the

²This content is available online at <<http://cnx.org/content/m23905/1.6/>>.

lattice parameters are temperature dependent (Figure 6.16). The lattice constant (a), in Å, for high purity silicon may be calculated for any temperature (T) over the temperature range 293 - 1073 K by the formula shown below.

$$a_T = 5.4304 + 1.8138 \times 10^{-5} (T - 298.15 \text{ K}) + 1.542 \times 10^{-9} (T - 298.15 \text{ K})^2$$

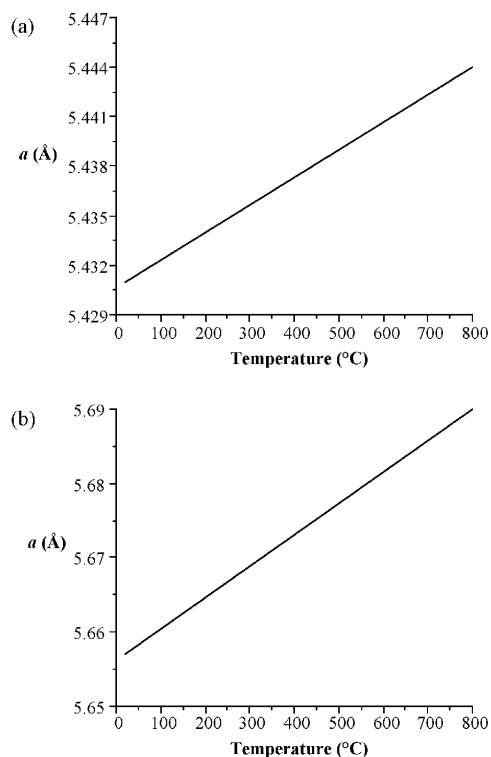


Figure 6.16: Temperature dependence of the lattice parameter for (a) Si and (b) Ge.

Even though the diamond cubic forms of Si and Ge are the only forms of direct interest to semiconductor devices, each exists in numerous crystalline high pressure and meta-stable forms. These are described along with their interconversions, in Table 6.4.

Phase	Structure	Remarks
Si I	diamond cubic	stable at normal pressure
Si II	grey tin structure	formed from Si I or Si V above 14 GPa
Si III	cubic	metastable, formed from Si II above 10 GPa
Si IV	hexagonal	
Si V	unidentified	stable above 34 GPa, formed from Si II above 16 GPa
Si VI	hexagonal close packed	stable above 45 GPa
Ge I	diamond cubic	low-pressure phase
Ge II	β -tin structure	formed from Ge I above 10 GPa
Ge III	tetragonal	formed by quenching Ge II at low pressure
Ge IV	body centered cubic	formed by quenching Ge II to 1 atm at 200 K

Table 6.4: High pressure and metastable phases of silicon and germanium.

6.2.3 Group III-V (13-15) compounds

The stable phases for the arsenides, phosphides and antimonides of aluminum, gallium and indium all exhibit zinc blende structures (Figure 6.17). In contrast, the nitrides are found as wurtzite structures (e.g., Figure 6.18). The structure, lattice parameters, and densities of the III-V compounds are given in Table 6.5. It is worth noting that contrary to expectation the lattice parameter of the gallium compounds is smaller than their aluminum homolog; for GaAs $a = 5.653 \text{ \AA}$; AlAs $a = 5.660 \text{ \AA}$. As with the group IV elements the lattice parameters are highly temperature dependent; however, additional variation arises from any deviation from absolute stoichiometry. These effects are shown in Figure 6.19.

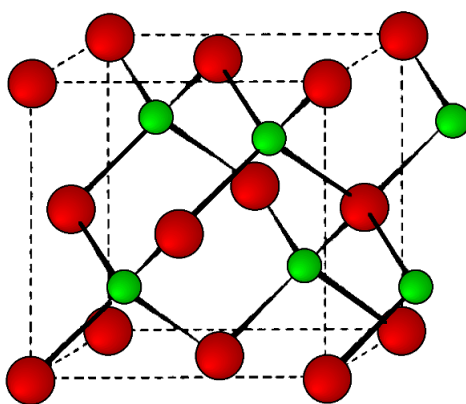


Figure 6.17: Unit cell structure of a zinc blende (ZnS) lattice. Zinc atoms are shown in green (small), sulfur atoms shown in red (large), and the dashed lines show the unit cell.

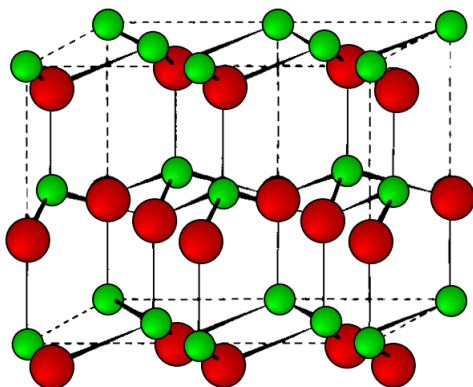


Figure 6.18: Unit cell structure of a wurtzite lattice. Zinc atoms are shown in green (small), sulfur atoms shown in red (large), and the dashed lines show the unit cell.

Compound	Structure	Lattice parameter ($\text{\AA}$)	Density (g/cm^3)
AlN	wurtzite	$a = 3.11(1), c = 4.98(1)$	3.255
AlP	zinc blende	$a = 5.4635(4)$	2.40(1)
AlAs	zinc blende	$a = 5.660$	3.760
AlSb	zinc blende	$a = 6.1355(1)$	4.26
GaN	wurtzite	$a = 3.190, c = 5.187$	
GaP	zinc blende	$a = 5.4505(2)$	4.138
GaAs	zinc blende	$a = 5.65325(2)$	5.3176(3)
InN	wurtzite	$a = 3.5446, c = 5.7034$	6.81
InP	zinc blende	$a = 5.868(1)$	4.81
InAs	zinc blende	$a = 6.0583$	5.667
InSb	zinc blende	$a = 6.47937$	5.7747(4)

Table 6.5: Lattice parameters and densities (measured at 298 K) for the III-V (13-15) compound semiconductors. Estimated standard deviations given in parentheses.

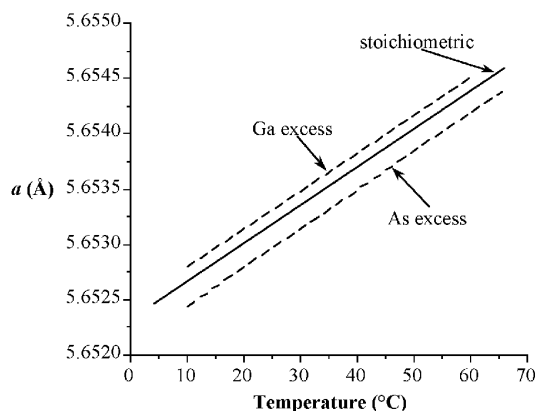


Figure 6.19: Temperature dependence of the lattice parameter for stoichiometric GaAs and crystals with either Ga or As excess.

The homogeneity of structures of alloys for a wide range of solid solutions to be formed between III-V compounds in almost any combination. Two classes of ternary alloys are formed: $\text{III}_x\text{-III}_{1-x}\text{-V}$ (e.g., $\text{Al}_x\text{-Ga}_{1-x}\text{-As}$) and $\text{III-V}_{1-x}\text{-V}_x$ (e.g., $\text{Ga-As}_{1-x}\text{-P}_x$). While quaternary alloys of the type $\text{III}_x\text{-III}_{1-x}\text{-V}_y\text{-V}_{1-y}$ allow for the growth of materials with similar lattice parameters, but a broad range of band gaps. A very important ternary alloy, especially in optoelectronic applications, is $\text{Al}_x\text{-Ga}_{1-x}\text{-As}$ and its lattice parameter (a) is directly related to the composition (x).

$$a = 5.6533 + 0.0078 x$$

Not all of the III-V compounds have well characterized high-pressure phases. However, in each case where a high-pressure phase is observed the coordination number of both the group III and group V element increases from four to six. Thus, AlP undergoes a zinc blende to rock salt transformation at high pressure above 170 kbar, while AlSb and GaAs form orthorhombic distorted rock salt structures above 77 and 172 kbar, respectively. An orthorhombic structure is proposed for the high-pressure form of InP (>133 kbar). Indium arsenide (InAs) undergoes two-phase transformations. The zinc blende structure is converted to a rock salt structure above 77 kbar, which in turn forms a β -tin structure above 170 kbar.

6.2.4 Group II-VI (12-16) compounds

The structures of the II-VI compound semiconductors are less predictable than those of the III-V compounds (above), and while zinc blende structure exists for almost all of the compounds there is a stronger tendency towards the hexagonal wurtzite form. In several cases the zinc blende structure is observed under ambient conditions, but may be converted to the wurtzite form upon heating. In general the wurtzite form predominates with the smaller anions (e.g., oxides), while the zinc blende becomes the more stable phase for the larger anions (e.g., tellurides). One exception is mercury sulfide (HgS) that is the archetype for the trigonal cinnabar phase. Table 6.6 lists the stable phase of the chalcogenides of zinc, cadmium and mercury, along with their high temperature phases where applicable. Solid solutions of the II-VI compounds are not as easily formed as for the III-V compounds; however, two important examples are $\text{ZnS}_x\text{Se}_{1-x}$ and $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$.

Compound	Structure	Lattice parameter ($\text{\AA}$)	Density (g/cm^3)
ZnS	zinc blende	$a = 5.410$	4.075
	wurtzite	$a = 3.822, c = 6.260$	4.087
ZnSe	Zinc blende	$a = 5.668$	5.27
ZnTe	Zinc blende	$a = 6.10$	5.636
CdS	wurtzite	$a = 4.136, c = 6.714$	4.82
CdSe	wurtzite	$a = 4.300, c = 7.011$	5.81
CdTe	Zinc blende	$a = 6.482$	5.87
HgS	cinnabar	$a = 4.149, c = 9.495$	
	Zinc blende	$a = 5.851$	7.73
HgSe	Zinc blende	$a = 6.085$	8.25
HgTe	Zinc blende	$a = 6.46$	8.07

Table 6.6: Lattice parameters and densities (measured at 298 K) for the II-VI (12-16) compound semiconductors.

The zinc chalcogenides all transform to a cesium chloride structure under high pressures, while the cadmium compounds all form rock salt high-pressure phases (Figure 6.20). Mercury selenide (HgSe) and mercury telluride (HgTe) convert to the mercury sulfide archetype structure, cinnabar, at high pressure.

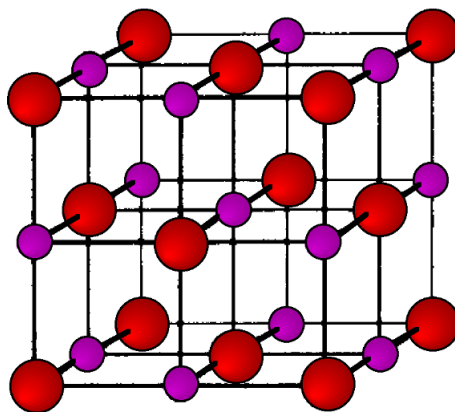


Figure 6.20: Unit cell structure of a rock salt lattice. Sodium ions are shown in purple and chloride ions are shown in red.

6.2.5 I-III-VI₂ (11-13-16) compounds

Nearly all I-III-VI₂ compounds at room temperature adopt the chalcopyrite structure (Figure 6.21). The cell constants and densities are given in Table 6.7. Although there are few reports of high temperature or

high-pressure phases, AgInS_2 has been shown to exist as a high temperature orthorhombic polymorph ($a = 6.954$, $b = 8.264$, and $c = 6.683$ Å), and AgInTe_2 forms a cubic phase at high pressures.

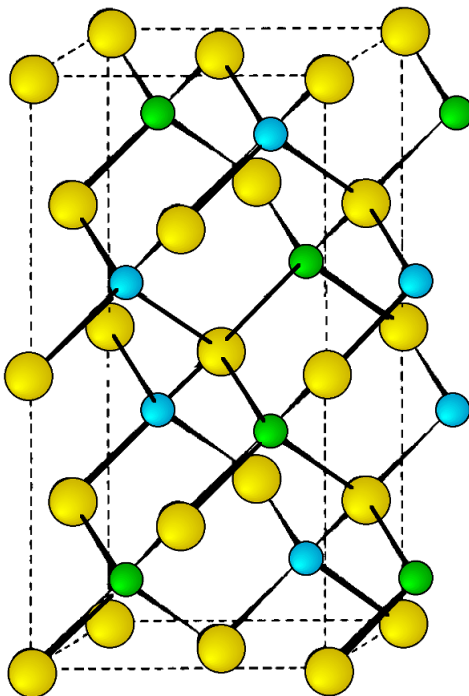


Figure 6.21: Unit cell structure of a chalcopyrite lattice. Copper atoms are shown in blue, iron atoms are shown in green and sulfur atoms are shown in yellow. The dashed lines show the unit cell.

Compound	Lattice parameter a (Å)	Lattice parameter c (Å)	Density (g.cm ³)
CuAlS ₂	5.32	10.430	3.45
CuAlSe ₂	5.61	10.92	4.69
CuAlTe ₂	5.96	11.77	5.47
CuGaS ₂	5.35	10.46	4.38
CuGaSe ₂	5.61	11.00	5.57
CuGaTe ₂	6.00	11.93	5.95
CuInS ₂	5.52	11.08	4.74
CuInSe ₂	5.78	11.55	5.77
CuInTe ₂	6.17	12.34	6.10
AgAlS ₂	6.30	11.84	6.15
AgGaS ₂	5.75	10.29	4.70
AgGaSe ₂	5.98	10.88	5.70
AgGaTe ₂	6.29	11.95	6.08
AgInS ₂	5.82	11.17	4.97
AgInSe ₂	6.095	11.69	5.82
AgInTe ₂	6.43	12.59	6.96

Table 6.7: Chalcopyrite lattice parameters and densities (measured at 298 K) for the I-III-VI compound semiconductors. Lattice parameters for tetragonal cell.

Of the I-III-VI₂ compounds, the copper indium chalcogenides (CuInE₂) are certainly the most studied for their application in solar cells. One of the advantages of the copper indium chalcogenide compounds is the formation of solid solutions (alloys) of the formula CuInE_{2-x}E'_x, where the composition variable (x) varies from 0 to 2. The CuInS_{2-x}Se_x and CuInSe_{2-x}Te_x systems have also been examined, as has the CuGa_yIn_{1-y}S_{2-x}Se_x quaternary system. As would be expected from a consideration of the relative ionic radii of the chalcogenides the lattice parameters of the CuInS_{2-x}Se_x alloy should increase with increased selenium content. Vergard's law requires the lattice constant for a linear solution of two semiconductors to vary linearly with composition (e.g., as is observed for Al_xGa_{1-x}As), however, the variation of the tetragonal lattice constants (a and c) with composition for CuInS_{2-x}S_x are best described by the parabolic relationships.

$$a = 5.532 + 0.0801 x + 0.0260 x^2$$

$$c = 11.156 + 0.1204 x + 0.0611 x^2$$

A similar relationship is observed for the CuInSe_{2-x}Te_x alloys.

$$a = 5.783 + 0.1560 x + 0.0212 x^2$$

$$c = 11.628 + 0.3340 x + 0.0277 x^2$$

The large difference in ionic radii between S and Te (0.37 Å) prevents formation of solid solutions in the CuInS_{2-x}Te_x system, however, the single alloy CuInS_{1.5}Te_{0.5} has been reported.

6.2.6 Orientation effects

Once single crystals of high purity silicon or gallium arsenide are produced they are cut into wafers such that the exposed face of these wafers is either the crystallographic {100} or {111} planes. The relative structure of these surfaces are important with respect to oxidation, etching and thin film growth. These processes are orientation-sensitive; that is, they depend on the direction in which the crystal slice is cut.

6.2.6.1 Atom density and dangling bonds

The principle planes in a crystal may be differentiated in a number of ways, however, the atom and/or bond density are useful in predicting much of the chemistry of semiconductor surfaces. Since both silicon and gallium arsenide are *fcc* structures and the {100} and {111} are the only technologically relevant surfaces, discussions will be limited to *fcc* {100} and {111}.

The atom density of a surface may be defined as the number of atoms per unit area. Figure 6.22 shows a schematic view of the {111} and {100} planes in a *fcc* lattice. The {111} plane consists of a hexagonal close packed array in which the crystal directions within the plane are oriented at 60° to each other. The hexagonal packing and the orientation of the crystal directions are indicated in Figure 6.22b as an overlaid hexagon. Given the intra-planar inter-atomic distance may be defined as a function of the lattice parameter, the area of this hexagon may be readily calculated. For example in the case of silicon, the hexagon has an area of $38.30 \text{ \AA}^2$. The number of atoms within the hexagon is three: the atom in the center plus $1/3$ of each of the six atoms at the vertices of the hexagon (each of the atoms at the hexagons vertices is shared by three other adjacent hexagons). Thus, the atom density of the {111} plane is calculated to be $0.0783 \text{ \AA}^{-2}$. Similarly, the atom density of the {100} plane may be calculated. The {100} plane consists of a square array in which the crystal directions within the plane are oriented at 90° to each other. Since the square is coincident with one of the faces of the unit cell the area of the square may be readily calculated. For example in the case of silicon, the square has an area of $29.49 \text{ \AA}^2$. The number of atoms within the square is 2: the atom in the center plus $1/4$ of each of the four atoms at the vertices of the square (each of the atoms at the corners of the square are shared by four other adjacent squares). Thus, the atom density of the {100} plane is calculated to be $0.0678 \text{ \AA}^{-2}$. While these values for the atom density are specific for silicon, their ratio is constant for all diamond cubic and zinc blende structures: {100}:{111} = 1:1.155. In general, the fewer dangling bonds the more stable a surface structure.

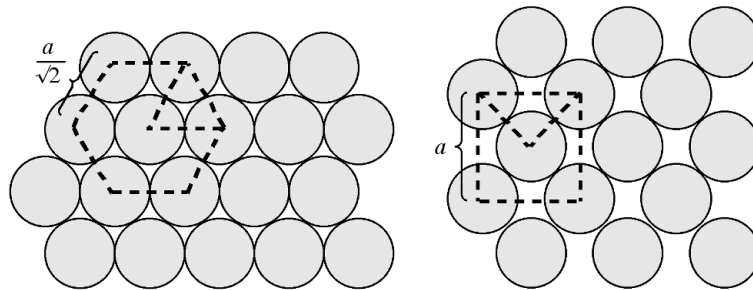


Figure 6.22: Schematic representation of the (111) and (100) faces of a face centered cubic (*fcc*) lattice showing the relationship between the close packed rows.

An atom inside a crystal of any material will have a coordination number (n) determined by the structure of the material. For example, all atoms within the bulk of a silicon crystal will be in a tetrahedral four-coordinate environment ($n = 4$). However, at the surface of a crystal the atoms will not make their full complement of bonds. Each atom will therefore have less nearest neighbors than an atom within the bulk of the material. The missing bonds are commonly called dangling bonds. While this description is not particularly accurate it is, however, widely employed and as such will be used herein. The number of dangling bonds may be defined as the difference between the ideal coordination number (determined by the bulk crystal structure) and the actual coordination number as observed at the surface.

Figure 6.23 shows a section of the {111} surfaces of a diamond cubic lattice viewed perpendicular to the

$\{111\}$ plane. The atoms within the bulk have a coordination number of four. In contrast, the atoms at the surface (e.g., the atom shown in blue in Figure 6.23) are each bonded to just three other atoms (the atoms shown in red in Figure 6.23), thus each surface atom has one dangling bond. As can be seen from Figure 6.24, which shows the atoms at the $\{100\}$ surface viewed perpendicular to the $\{100\}$ plane, each atom at the surface (e.g., the atom shown in blue in Figure 6.24) is only coordinated to two other atoms (the atoms shown in red in Figure 6.24), leaving two dangling bonds per atom. It should be noted that the same number of dangling bonds are found for the $\{111\}$ and $\{100\}$ planes of a zinc blende lattice. The ratio of dangling bonds for the $\{100\}$ and $\{111\}$ planes of all diamond cubic and zinc blende structures is $\{100\}:\{111\} = 2:1$. Furthermore, since the atom densities of each plane are known then the ratio of the dangling bond densities is determined to be: $\{100\}:\{111\} = 1:0.577$.

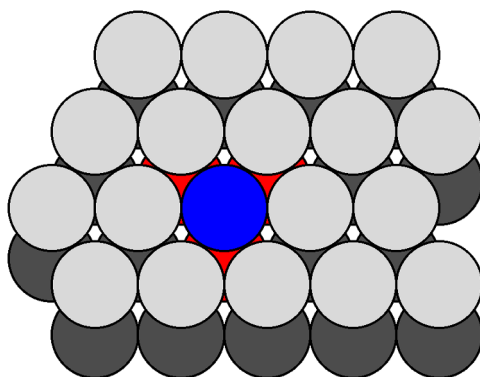


Figure 6.23: A section of the $\{111\}$ surfaces of a diamond cubic lattice viewed perpendicular to the $\{111\}$ plane.

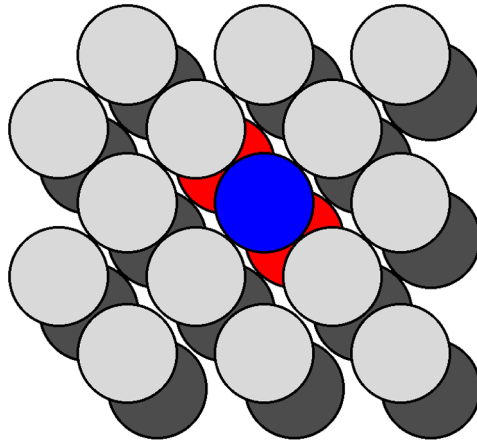


Figure 6.24: A section of the $\{100\}$ surface of a diamond cubic lattice viewed perpendicular to the $\{100\}$ plane.

6.2.6.2 Silicon

For silicon, the $\{111\}$ planes are closer packed than the $\{100\}$ planes. As a result, growth of a silicon crystal is therefore slowest in the $\langle 111 \rangle$ direction, since it requires laying down a close packed atomic layer upon another layer in its closest packed form. As a consequence $\langle 111 \rangle$ Si is the easiest to grow, and therefore the least expensive.

The dissolution or etching of a crystal is related to the number of broken bonds already present at the surface: the fewer bonds to be broken in order to remove an individual atom from a crystal, the easier it will be to dissolve the crystal. As a consequence of having only one dangling bond (requiring three bonds to be broken) etching silicon is slowest in the $\langle 111 \rangle$ direction. The electronic properties of a silicon wafer are also related to the number of dangling bonds.

Silicon microcircuits are generally formed on a single crystal wafer that is diced after fabrication by either sawing part way through the wafer thickness or scoring (scribing) the surface, and then physically breaking. The physical breakage of the wafer occurs along the natural cleavage planes, which in the case of silicon are the $\{111\}$ planes.

6.2.6.3 Gallium arsenide

The zinc blende lattice observed for gallium arsenide results in additional considerations over that of silicon. Although the $\{100\}$ plane of GaAs is structurally similar to that of silicon, two possibilities exist: a face consisting of either all gallium atoms or all arsenic atoms. In either case the surface atoms have two dangling bonds, and the properties of the face are independent of whether the face is gallium or arsenic.

The $\{111\}$ plane also has the possibility of consisting of all gallium or all arsenic. However, unlike the $\{100\}$ planes there is a significant difference between the two possibilities. Figure 6.17 shows the gallium arsenide structure represented by two interpenetrating *fcc* lattices. The $[111]$ axis is vertical within the plane of the page. Although the structure consists of alternate layers of gallium and arsenic stacked along the $[111]$ axis, the distance between the successive layers alternates between large and small. Assigning arsenic as the parent lattice the order of the layers in the $[111]$ direction is As-Ga-As-Ga-As-Ga, while in the $\begin{bmatrix} \bar{1} & \bar{1} & \bar{1} \end{bmatrix}$

direction the layers are ordered, Ga-As-Ga-As-Ga-As (Figure 6.25). In silicon these two directions are of course identical. The surface of a crystal would be either arsenic, with three dangling bonds, or gallium, with one dangling bond. Clearly, the latter is energetically more favorable. Thus, the (111) plane shown in Figure 6.25 is called the (111) Ga face. Conversely, the $\left[\begin{smallmatrix} \bar{\bar{\bar{1}}} \\ \bar{\bar{1}} \\ \bar{1} \end{smallmatrix}\right]$ plane would be either gallium, with three dangling bonds, or arsenic, with one dangling bond. Again, the latter is energetically more favorable and the $\left[\begin{smallmatrix} \bar{\bar{\bar{1}}} \\ \bar{\bar{1}} \\ \bar{1} \end{smallmatrix}\right]$ plane is therefore called the (111) As face.

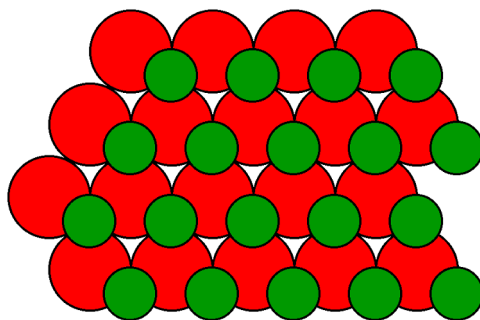


Figure 6.25: The (111) Ga face of GaAs showing a surface layer containing gallium atoms (green) with one dangling bond per gallium and three bonds to the arsenic atoms (red) in the lower layer.

The (111) As is distinct from that of (111) Ga due to the difference in the number of electrons at the surface. As a consequence, the (111) As face etches more rapidly than the (111) Ga face. In addition, surface evaporation below 770 °C occurs more rapidly at the (111) As face.

6.2.7 Bibliography

- M. Baublitz and A. L. Ruoff, *J. Appl. Phys.*, 1982, **53**, 6179.
- J. C. Jamieson, *Science*, 1963, **139**, 845.
- C. C. Landry, J. Lockwood, and A. R. Barron, *Chem. Mater.*, 1995, **7**, 699.
- M. Robbins, J. C. Phillips, and V. G. Lambrecht, *J. Phys. Chem. Solids*, 1973, **34**, 1205.
- D. Sridevi and K. V. Reddy, *Mat. Res. Bull.*, 1985, **20**, 929.
- Y. K. Vohra, S. T. Weir, and A. L. Ruoff, *Phys. Rev. B*, 1985, **31**, 7344.
- W. M. Yin and R. J. Paff, *J. Appl. Phys.*, 1973, **45**, 1456.

6.3 X-ray Crystallography

6.3.1 An Introduction to X-ray Diffraction³

6.3.1.1 History of X-ray crystallography

The birth of X-ray crystallography is considered by many to be marked by the formulation of the *law of constant angles* by Nicolaus Steno in 1669 (Figure 6.26). Although Steno is well known for his numerous

³This content is available online at <<http://cnx.org/content/m38289/1.1/>>.

principles regarding all areas of life, this particular law dealing with geometric shapes and crystal lattices is familiar ground to all chemists. It simply states that *the angles between corresponding faces on crystals are the same for all specimens of the same mineral*. The significance of this for chemistry is that given this fact, crystalline solids will be easily identifiable once a database has been established. Much like solving a puzzle, crystal structures of heterogeneous compounds could be solved very methodically by comparison of chemical composition and their interactions.



Figure 6.26: Danish pioneer in both anatomy and geology Nicolas Steno (1638 – 1686).

Although Steno was given credit for the notion of crystallography, the man that provided the tools necessary to bring crystallography into the scientific arena was Wilhelm Roentgen (Figure 6.27), who in 1895 successfully pioneered a new form of photography, one that could allegedly penetrate through paper, wood, and human flesh; due to a lack of knowledge of the specific workings of this new discovery, the scientific community conveniently labeled the new particles *X-rays*. This event set off a chain reaction of experiments and studies, not all performed by physicists. Within one single month, medical doctors were using X-rays to pinpoint foreign objects such in the human body such as bullets and kidney stones (Figure 6.28).



Figure 6.27: German physicist Wilhelm Conrad Röntgen (1845 – 1923).



Figure 6.28: First public X-ray image ever produced. Pictured is the left hand of Anna Berthe Röntgen. The uncharacteristic bulge is her ring.

The credit for the actual discovery of X-ray diffraction goes to Max von Laue (Figure 6.29), to whom the Nobel Prize in physics in 1914 was awarded for the discovery of the diffraction of X-rays. Legend has it that the notion that eventually led to a Nobel prize was born in a garden in Munich, while von Laue was pondering the problem of passing waves of electromagnetic radiation through a specific crystalline arrangement of atoms. Because of the relatively large wavelength of visible light, von Laue was forced to turn his attention to another part of the electromagnetic spectrum, to where shorter wavelengths resided. Only a few decades earlier, Röntgen had publicly announced the discovery of X-rays, which supposedly had a wavelength shorter than that of visible light. Having this information, von Laue entrusted the task of performing the experimental work to two technicians, Walter Friedrich and Paul Knipping. The setup consisted of an X-ray source, which beamed radiation directly into a copper sulfate crystal housed in a lead box. Film was lined against the sides and back of the box, so as to capture the X-ray beam and its diffraction pattern. Development of the film showed a dark circle in the center of the film, surrounded by several extremely well defined circles, which had formed as a result of the diffraction of the X-ray beam by the ordered geometric arrangement of copper sulfate. Max von Laue then proceeded to work out the mathematical formulas involved in the observed diffraction pattern, for which he was awarded the Nobel Prize in physics in 1914.



Figure 6.29: German physicist Max Theodor Felix von Laue (1879 – 1960) won the Nobel Prize for discovery of the diffraction of X-rays by crystals.

6.3.1.2 Principles of X-ray diffraction (XRD)

The simplest definition of diffraction is *the irregularities caused when waves encounter an object*. Diffraction is a phenomenon that exists commonly in everyday activities, but is often disregarded and taken for granted. For example, when looking at the information side of a compact disc, a rainbow pattern will often appear when it catches light at a certain angle. This is caused by visible light striking the grooves of the disc, thus producing a rainbow effect (Figure 6.30), as interpreted by the observers' eyes. Another example is the formation of seemingly concentric rings around an astronomical object of significant luminosity when

observed through clouds. The particles that make up the clouds diffract light from the astronomical object around its edges, causing the illusion of rings of light around the source. It is easy to forget that diffraction is a phenomenon that applies to all forms of waves, not just electromagnetic radiation. Due to the large variety of possible types of diffractions, many terms have been coined to differentiate between specific types. The most prevalent type of diffraction to X-ray crystallography is known as Bragg diffraction, which is defined as the scattering of waves from a crystalline structure.



Figure 6.30: The rainbow effects caused by visible light striking the grooves of a compact disc (CD).

Formulated by William Lawrence Bragg (Figure 6.31), the equation of Bragg's law relates wavelength to angle of incidence and lattice spacing, (6.10), where n is a numeric constant known as the order of the diffracted beam, λ is the wavelength of the beam, d denotes the distance between lattice planes, and θ represents the angle of the diffracted wave. The conditions given by this equation must be fulfilled if diffraction is to occur.

$$n\lambda = 2d \sin(\theta) \tag{6.10}$$

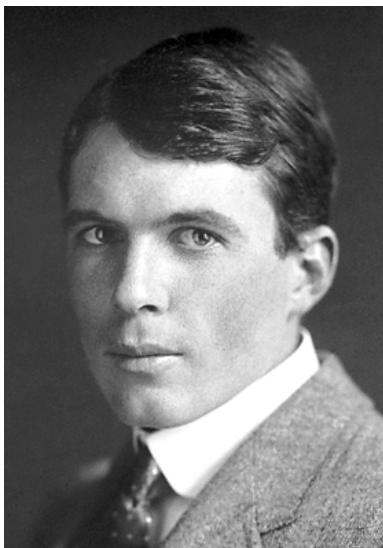


Figure 6.31: Australian-born British physicist Sir William Lawrence Bragg (1890 – 1971).

Because of the nature of diffraction, waves will experience either constructive (Figure 6.32) or destructive (Figure 6.33) interference with other waves. In the same way, when an X-ray beam is diffracted off a crystal, the different parts of the diffracted beam will have seemingly stronger energy, while other parts will have seemed to lost energy. This is dependent mostly on the wavelength of the incident beam, and the spacing between crystal lattices of the sample. Information about the lattice structure is obtained by varying beam wavelengths, incident angles, and crystal orientation. Much like solving a puzzle, a three dimensional structure of the crystalline solid can be constructed by observing changes in data with variation of the aforementioned variables

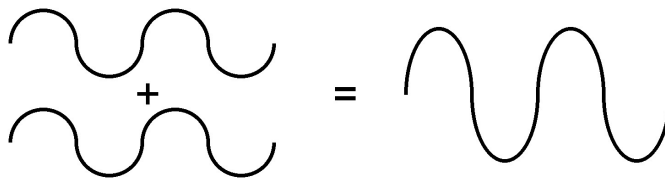


Figure 6.32: Schematic representation of constructive interference.

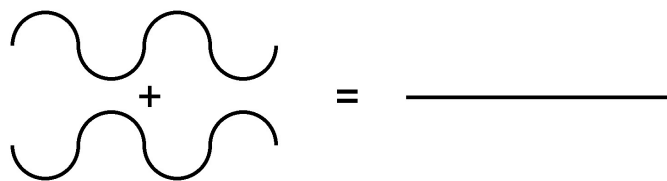


Figure 6.33: Schematic representation of destructive interference.

6.3.1.3 The X-ray diffractometer

At the heart of any XRD machine is the X-ray source. Modern day machines generally rely on copper metal as the element of choice for producing X-rays, although there are variations among different manufacturers. Because diffraction patterns are recorded over an extended period of time during sample analysis, it is very important that beam intensity remain constant throughout the entire analysis, or else faulty data will be procured. In light of this, even before an X-ray beam is generated, current must pass through a voltage regular, which will guarantee a steady stream of voltage to the X-ray source.

Another crucial component to the analysis of crystalline via X-rays is the detector. When XRD was first developed, film was the most commonly used method for recognizing diffraction patterns. The most obvious disadvantage to using film is the fact that it has to be replaced every time a new specimen is introduced, making data collection a time consuming process. Furthermore, film can only be used once, leading to an increase in cost of operating diffraction analysis.

Since the origins of XRD, detection methods have progressed to the point where modern XRD machines are equipped with semiconductor detectors, which produce pulses proportional to the energy absorbed. With these modern detectors, there are two general ways in which a diffraction pattern may be obtained. The first is called continuous scan, and it is exactly what the name implies. The detector is set in a circular motion around the sample, while a beam of X-ray is constantly shot into the sample. Pulses of energy are plotted with respect to diffraction angle, which ensure all diffracted X-rays are recorded. The second and more widely used method is known as step scan. Step scanning bears similarity to continuous scan, except it is highly computerized and much more efficient. Instead of moving the detector in a circle around the entire sample, step scanning involves collecting data at one fixed angle at a time, thus the name. Within these detection parameters, the types of detectors can themselves be varied. A more common type of detector, known as the charge-coupled device (CCD) detector (Figure 6.34), can be found in many XRD machines, due to its fast data collection capability. A CCD detector is comprised of numerous radiation sensitive grids, each linked to sensors that measure changes in electromagnetic radiation. Another commonly seen type of detector is a simple scintillation counter (Figure 6.35), which counts the intensity of X-rays that it encounters as it moves along a rotation axis. A comparable analogy to the differences between the two detectors mentioned would be that the CCD detector is able to see in two dimensions, while scintillation counters are only able to see in one dimension.



Figure 6.34: Single crystal X-ray diffractometer with a CCD detector. The incident beam is generated and delivered through the silver apparatus on the right side of the sample, and the detector is the large black camera to the left of the sample.

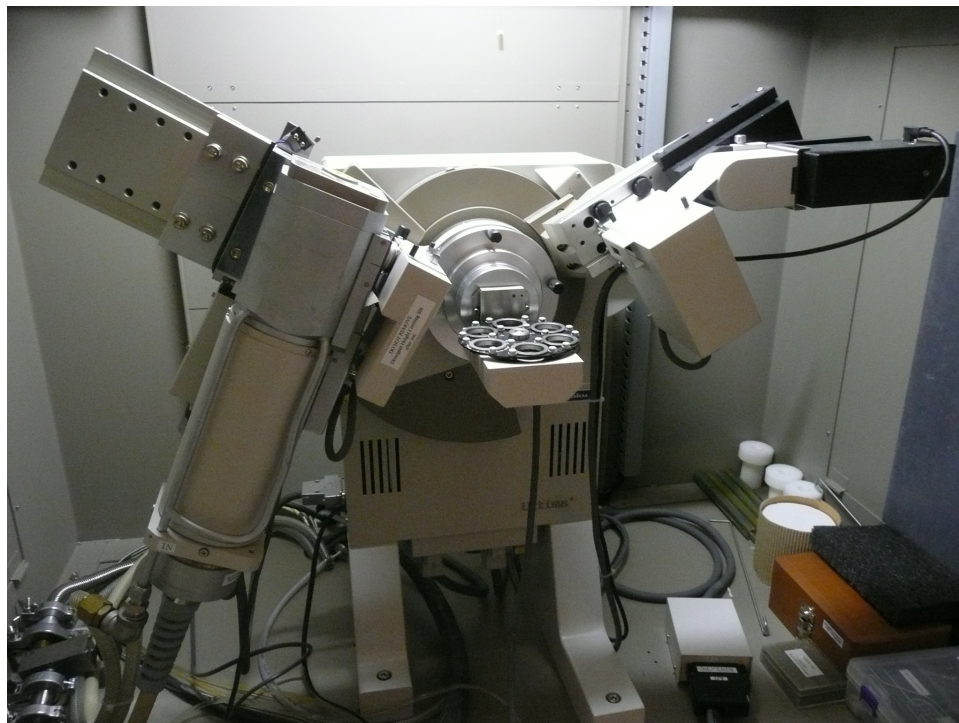


Figure 6.35: Image of a powder X-ray diffractometer. The incident beam enters from the tube on the left, and the detector is housed in the black box on the right side of the machine. This particular XRD machine is capable of handling six samples at once, and is fully automated from sample to sample.

Aside from the above two components, there are many other variables involved in sample analysis by an XRD machine. As mentioned earlier, a steady incident beam is extremely important for good data collection. To further ensure this, there will often be what is known as a Soller slit found in many XRD machines. A Soller slit acts much like polarized sunglasses: it organizes random X-ray beams into a stack of neatly arranged waves parallel to the plane of rotation of the detector. Some machines have a Soller slit between the sample and the detector, which drastically reduces the amount of background noise, especially when analyzing iron samples with a copper X-ray source.

This single crystal XRD machine (Figure 6.34) features a cooling gas line, which allows the user to bring down the temperature of a sample considerably below room temperature. Doing so allows for the opportunities for studies performed where the sample is kept in a state of extremely low energy, negating a lot of vibrational motion that might interfere with consistent data collection of diffraction patterns. Furthermore, information can be collected on the effects of temperature on a crystal structure. Also seen in Figure 6.34 is the hook-shaped object located between the beam emitter and detector. It serves the purpose of blocking X-rays that were not diffracted from being seen by the detector, drastically reducing the amount of unnecessary noise that would otherwise obscure data analysis.

6.3.1.4 Evolution of powder XRD

Over time, XRD analysis has evolved from a very narrow and specific field to something that encompasses a much wider branch of the scientific arena. In its early stages, XRD was (with the exception of the simplest

structures) confined to single crystal analysis, as detection methods had not advanced to a point where more complicated procedures were able to be performed. After many years of discovery and refining, however, technology has progressed to where crystalline properties (structure) of solids can be gleaned directly from a powder sample, thus offering information for samples that cannot be obtained as a single crystal. One area in which this is particularly useful is pharmaceuticals, since many of the compounds studied are not available in single crystal form, only in a powder.

Even though single crystal diffraction and powder diffraction essentially generate the same data, due to the powdered nature of the latter sample, diffraction lines will often overlap and interfere with data collection. This is apparently especially when the diffraction angle 2θ is high; patterns that emerge will be almost to the point of unidentifiable, because of disruption of individual diffraction patterns. For this particular reason, a new approach to interpreting powder diffraction data has been created.

There are two main methods for interpreting diffraction data:

- The first is known as the traditional method, which is very straightforward, and bears resemblance to single crystal data analysis. This method involves a two step process: 1) the intensities and diffraction patterns from the sample is collected, and 2) the data is analyzed to produce a crystalline structure. As mentioned before, however, data from a powdered sample is often obscured by multiple diffraction patterns, which decreases the chance that the generated structure is correct.
- The second method is called the direct-space approach. This method takes advantage of the fact that with current technology, diffraction data can be calculated for any molecule, whether or not it is the molecule in question. Even before the actual diffraction data is collected, a large number of theoretical patterns of suspect molecules are generated by computer, and compared to experimental data. Based on correlation and how well the theoretical pattern fits the experimental data best, a guess is formulated to which compound is under question. This method has been taken a step further to mimic social interactions in a community. For example, first generation theoretical trial molecules, after comparison with the experimental data, are allowed to evolve within parameters set by researchers. Furthermore, if appropriate, molecules are produce offspring with other molecules, giving rise to a second generation of molecules, which fit the experimental data even better. Just like a natural environment, genetic mutations and natural selection are all introduced into the picture, ultimately giving rise a molecular structure that represents data collected from XRD analysis.

Another important aspect of being able to study compounds in powder form for the pharmaceutical researcher is the ability to identify structures in their natural state. A vast majority of drugs in this day and age are delivered through powdered form, either in the form of a pill or a capsule. Crystallization processes may often alter the chemical composition of the molecule (e.g., by the inclusion of solvent molecules), and thus marring the data if confined to single crystal analysis. Furthermore, when the sample is in powdered form, there are other variables that can be adjusted to see real-time effects on the molecule. Temperature, pressure, and humidity are all factors that can be changed in-situ to glean data on how a drug might respond to changes in those particular variables.

6.3.1.5 Bibliography

- H. D. Jakubke and H. Jeschkeit, *Concise Encyclopedia Chemistry*, Walter de Gruyter, Berlin (1993).
- M. von Laue, *Concerning the detection of X-ray interferences*, Nobel Prize. Nobel Foundation (1915).
- K. Harris, *Am. Pharmaceut. Rev.*, 2004, **7.2**, 86.
- B. D. Cullity and S. R. Stock. *Elements of X-ray Diffraction*, 3rd Edition, Prentice Hall, New Jersey (2001).

6.3.2 Refinement of Crystallographic Disorder in the Tetrafluoroborate Anion⁴

6.3.2.1 Introduction

Through the course of our structural characterization of various tetrafluoroborate salts, the complex cation has nominally been the primary subject of interest; however, we observed that the tetrafluoroborate anion (BF_4^-) anions were commonly disordered (13 out of 23 structures investigated). Furthermore, a consideration of the Cambridge Structural Database as of 14th December 2010 yielded 8,370 structures in which the tetrafluoroborate anion is present; of these, 1044 (12.5%) were refined as having some kind of disorder associated with the BF_4^- anion. Several different methods have been reported for the treatment of these disorders, but the majority was refined as a non-crystallographic rotation along the axis of one of the B-F bonds.

Unfortunately, the very property that makes fluoro-anions such good candidates for non-coordinating counter-ions (i.e., weak intermolecular forces) also facilitates the presence of disorder in crystal structures. In other words, the appearance of disorder is intensified with the presence of a weakly coordinating spherical anion (e.g., BF_4^- or PF_6^-) which lack the strong intermolecular interactions needed to keep a regular, repeating anion orientation throughout the crystal lattice. Essentially, these weakly coordinating anions are loosely defined electron-rich spheres. All considered it seems that fluoro-anions, in general, have a propensity to exhibit apparently large atomic displacement parameters (ADP's), and thus, are appropriately refined as having fractional site-occupancies.

6.3.2.2 Refining disorder

In crystallography the observed atomic displacement parameters are an average of millions of unit cells throughout entire volume of the crystal, and thermally induced motion over the time used for data collection. A disorder of atoms/molecules in a given structure can manifest as flat or non-spherical atomic displacement parameters in the crystal structure. Such cases of disorder are usually the result of either thermally induced motion during data collection (i.e., *dynamic disorder*), or the *static disorder* of the atoms/molecules throughout the lattice. The latter is defined as the situation in which certain atoms, or groups of atoms, occupy slightly different orientations from molecule to molecule over the large volume (relatively speaking) covered by the crystal lattice. This static displacement of atoms can simulate the effect of thermal vibration on the scattering power of the "average" atom. Consequently, differentiation between thermal motion and static disorder can be ambiguous, unless data collection is performed at low temperature (which would negate much of the thermal motion observed at room temperature).

In most cases, this disorder is easily resolved as some non-crystallographic symmetry elements acting locally on the weakly coordinating anion. The atomic site occupancies can be refined using the FVAR instruction on the different parts (see PART 1 and PART 2 in Figure 6.36) of the disorder, having a site occupancy factor (s.o.f.) of x and $1-x$, respectively. This is accomplished by replacing 11.000 (on the F-atom lines in the "NAME.INS" file) with 21.000 or -21.000 for each of the different parts of the disorder. For instance, the "NAME.INS" file would look something like that shown in Figure 6.36. Note that for more heavily disordered structures, i.e., those with more than two disordered parts, the SUMP command can be used to determine the s.o.f. of parts 2, 3, 4, etc. the combined sum of which is set at s.o.f. = 1.0. These are designated in FVAR as the second, third, and fourth terms.

⁴This content is available online at <<http://cnx.org/content/m36687/1.3/>>.

```

ISOR      $F
ISOR      $F
DELU      $F
SADI      B(1) F(1A)  B(1) F(2A)  B(1) F(3A)  B(1) F(4A)
SADI      B(1) F(1B)  B(1) F(2B)  B(1) F(3B)  B(1) F(4B)
SADI      F(1A) F(2A)  F(1A) F(3A)  F(1A) F(4A)  etc.
SADI      F(1B) F(2B)  F(1B) F(3B)  F(1B) F(4B)  etc.
FVAR      0.1          0.5 a
B(1)      3            x            y            z            Ueq            11.000
PART 1a
F(1A)     6            x1          y1          z1          Ueq            21.000
F(2A)     6            x2          y2          z2          Ueq            21.000
F(3A)     6            x3          y3          z3          Ueq            21.000
F(4A)     6            x4          y4          z4          Ueq            21.000
PART 2
F(1B)     6            x1          y1          z1          Ueq            -21.000
F(2B)     6            x2          y2          z2          Ueq            -21.000
F(3B)     6            x3          y3          z3          Ueq            -21.000
F(4B)     6            x4          y4          z4          Ueq            -21.000
PART 0

```

Figure 6.36: General layout of the SHELXTL "NAME.INS" file for treatment of disordered tetrafluoroborate. ^a For more than two site occupancies "SUMP = 1.0 0.01 1.0 2 1.0 3 1.0 4" is added in addition to the FVAR instruction.

In small molecule refinement, the case will inevitably arise in which some kind of restraints or constraints must be used to achieve convergence of the data. A restraint is any additional information concerning a given structural feature, i.e., limits on the possible values of parameters, may be added into the refinement, thereby increasing the number of refined parameters. For example, aromatic systems are essentially flat, so for refinement purposes, a troublesome ring system could be restrained to lie in one plane. Restraints are not exact, i.e., they are tied to a probability distribution, whereas constraints are exact mathematical conditions. Restraints can be regarded as falling into one of several general types:

- Geometric restraints, which relates distances that should be similar.
- Rigid group restraints.
- Anti-bumping restraints.
- Linked parameter restraints.
- Similarity restraints.
- ADP restraints (Figure 6.37).
- Sum and average restraints.
- Origin fixing and shift limiting restraints.
- Those imposed upon atomic displacement parameters.

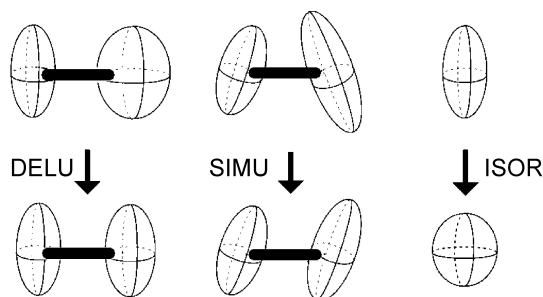


Figure 6.37: Consequence of the anisotropic displacement parameter (ADP) restraints DELU, SIMU, and ISOR on the shape and directionality of atomic displacement parameters. Adapted from P. Müller, *Crystal Structure Refinement, A Crystallographer's Guide to SHELXL*, Oxford University Press, UK (2006).

6.3.2.2.1 Geometric restraints

- SADI - similar distance restraints for named pairs of atoms.
- DFIX - defined distance restraint between covalently bonded atoms.
- DANG - defined non-bonding distance restraints, e.g., between F atoms belonging to the same PART of a disordered BF_4^- .
- FLAT - restrains group of atoms to lie in a plane.

6.3.2.2.2 Anisotropic displacement parameter restraints

- DELU - rigid bond restraints (Figure 6.37).
- SIMU - similar ADP restraints on corresponding U_{ij} components to be approximately equal for atoms in close proximity (Figure 6.37).
- ISOR - treat named anisotropic atoms to have approximately isotropic behavior (Figure 6.37).

6.3.2.2.3 Constraints (different than "restraints")

- EADP - equivalent atomic displacement parameters.
- AFIX - fitted group; e.g., AFIX 66 would fit the next six atoms into a regular hexagon.
- HFIX - places H atoms in geometrically ideal positions, e.g., HFIX 123 would place two sets of methyl H atoms disordered over two sites, 180° from each other.

6.3.2.3 Classes of disorder for the tetrafluoroborate anion

6.3.2.3.1 Rotation about a non-crystallographic axis along a B-F bond

The most common case of disorder is a rotation about an axis, the simplest of which involves a non-crystallographic symmetry related rotation axis about the vector made by one of the B-F bonds; this operation leads to three of the four F-atoms having two site occupancies (Figure 6.38). This disorder is also seen for ^tBu and CF_3 groups, and due to the C_3 symmetry of the $\text{C}(\text{CH}_3)_3$, CF_3 and BF_3 moieties actually results in a near C_2 rotation.

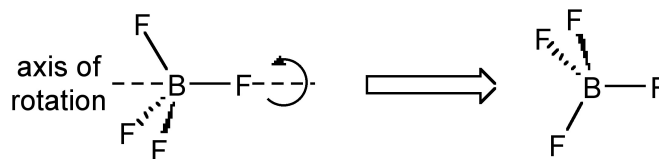


Figure 6.38: Schematic representation of the rotational relationship between two disordered orientations of the BF_4^- anion.

In a typical example, the BF_4^- anion present in the crystal structure of $[\text{H}(\text{Mes-dpa})]\text{BF}_4$ (Figure 6.39) was found to have a 75:25 site occupancy disorder for three of the four fluorine atoms (Figure 6.40). The disorder is a rotation about the axis of the $\text{B}(1)\text{-F}(1)$ bond. For initial refinement cycles, similar distance restraints (SADI) were placed on all B-F and F-F distances, in addition to similar ADP restraints (SIMU) and rigid bond restraints (DELU) for all F atoms. Restraints were lifted for final refinement cycles. A similar disorder refinement was required for $[\text{H}(2\text{-}^i\text{PrPh-dpa})]\text{BF}_4$ (45:55), while refinement of the disorder in $[\text{Cu}(2\text{-}^i\text{PrPh-dpa})(\text{styrene})]\text{BF}_4$ (65:35) was performed with only SADI and DELU restraints were lifted in final refinement cycles.

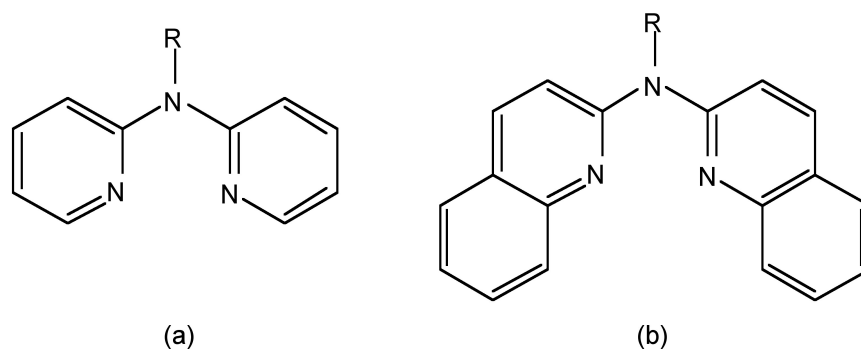


Figure 6.39: Structures of (a) substituted *bis*(2-pyridyl)amines (R-dpa) and (b) substituted *bis*(2-quinolyl)amines $[\text{R-N}(\text{quin})_2]$ ligands.

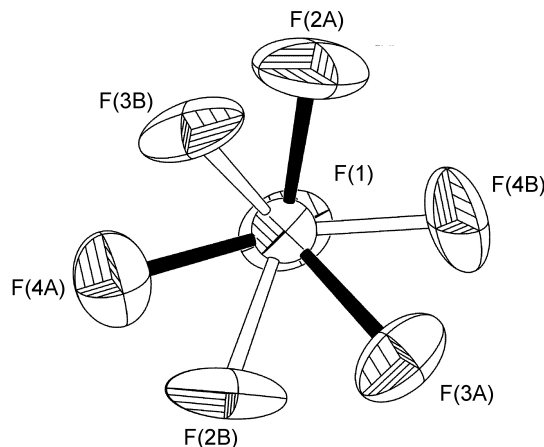


Figure 6.40: Structure for the BF_4^- anion in compound $[\text{H}(\text{Mes-dpa})]\text{BF}_4$ with both parts of the disorder present. Thermal ellipsoids are shown at the 20% level. Adapted from J. J. Allen, C. E. Hamilton, and A. R. Barron, *Dalton Trans.*, 2010, 11451.

In the complex $[\text{Ag}(\text{H-dpa})(\text{styrene})]\text{BF}_4$ use of the free variable (FVAR) led to refinement of disordered fluorine atoms F(2A)-F(4A) and F(2B)-F(4B) as having a 75:25 site-occupancy disorder (Figure 6.41). For initial refinement cycles, all B-F bond lengths were given similar distance restraints (SADI). Similar distance restraints (SADI) were also placed on F...F distances for each part, i.e., $\text{F}(2\text{A}) \cdots \text{F}(3\text{A}) = \text{F}(2\text{B}) \cdots \text{F}(3\text{B})$, etc. Additionally, similar ADP restraints (SIMU) and rigid bond restraints (DELU) were placed on all F atoms. All restraints, with the exception of SIMU, were lifted for final refinement cycles.

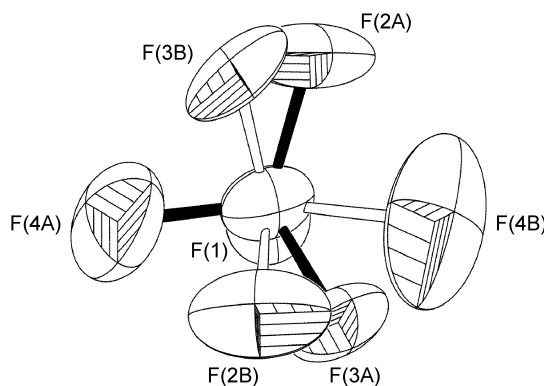


Figure 6.41: Structure of the disordered BF_4^- anion in $[\text{Ag}(\text{H-dpa})(\text{styrene})]\text{BF}_4$ viewed down the axis of disorder. Thermal ellipsoids are shown at the 30% probability level. Adapted from J. J. Allen and A. R. Barron, *J. Chem. Cryst.*, 2009, **39**, 935.

6.3.2.3.2 Rotation about a non-crystallographic axis not along a B-F bond

The second type of disorder is closely related to the first, with the only difference being that the rotational axis is tilted slightly off the B-F bond vector, resulting in all four F-atoms having two site occupancies (Figure 6.42). Tilt angles range from 6.5° to 42° .

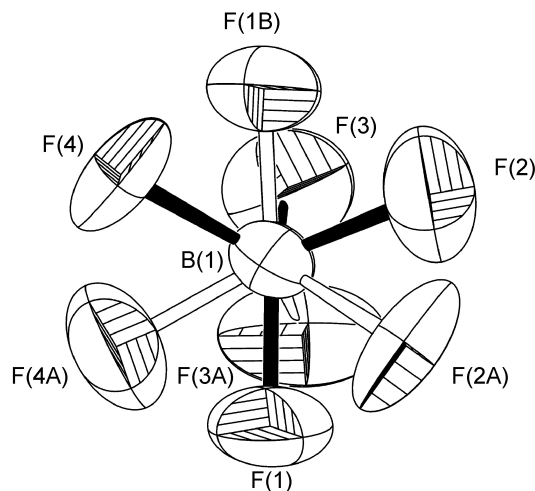


Figure 6.42: Molecular structure for the anion in $[\text{Cu}(\text{H-dpa})(\text{cis-3-octene})]\text{BF}_4$ with both parts of the disordered BF_4^- present. Thermal ellipsoids are shown at the 20% level. Adapted from J. J. Allen and A. R. Barron, *Dalton Trans.*, 2009, 878.

The disordered BF_4^- anion present in the crystal structure of $[\text{Cu}(\text{Ph-dpa})(\text{styrene})]\text{BF}_4$ was refined having fractional site occupancies for all four fluorine atoms about a rotation slightly tilted off the B(1)-F(2A) bond. However, it should be noted that while the $U_{\text{(eq)}}$ values determined for the data collected at low temperature data is roughly half that of that found at room temperature, as is evident by the sizes and shapes of fluorine atoms in Figure 6.43, the site occupancies were refined to 50:50 in each case, and there was no resolution in the disorder.

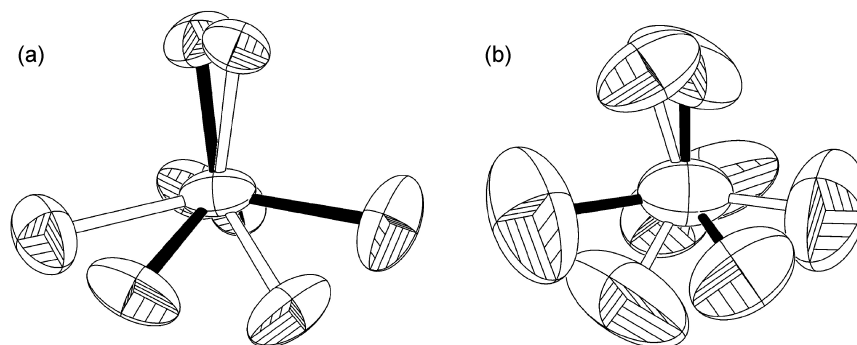


Figure 6.43: Comparison of the atomic displacement parameters observed in the disordered BF_4^- anion from $[\text{Cu}(\text{Ph-dpa})(\text{styrene})]\text{BF}_4$ at data collection temperature (a) $T = 213 \text{ K}$ and (b) $T = 298 \text{ K}$. Thermal ellipsoids are set at the 25% level.

An extreme example of rotation off-axis is observed where refinement of more than two site occupancies (Figure 6.44) with as many as thirteen different fluorine atom locations on only one boron atom.

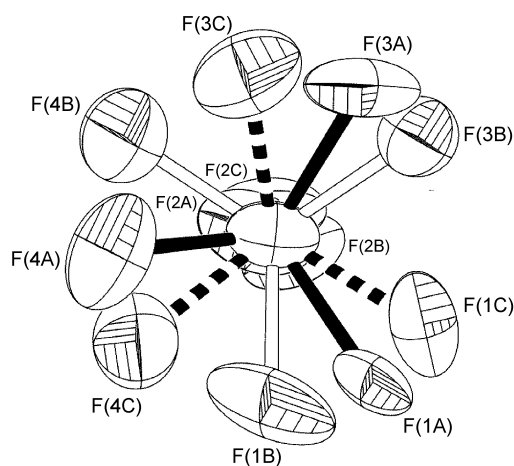


Figure 6.44: Structure for the tetrafluoroborate anion with twelve fluorine atom locations. Adapted from S. Martinez-Vargas, R. Toscano, and J. Valdez-Martinez, *Acta Cryst.*, 2007, **E63**, m1975.

6.3.2.3.3 Constrained rotation about a non-crystallographic axis not along a B-F bond

Although a wide range of tilt angles are possible, in some systems the angle is constrained by the presence of hydrogen bonding. For example, the BF_4^- anion present in $[\text{Cu}(\text{Mes-dpa})(\mu\text{-OH})(\text{H}_2\text{O})]_2[\text{BF}_4]_2$ was found to have a 60:40 site occupancy disorder of the four fluorine atoms, and while the disorder is a C_2 -rotation

slightly tilted off the axis of the B(1)-F(1A) bond, the angle is restricted by the presence of two B-F $\cdots$ O interactions for one of the isomers (Figure 6.45).

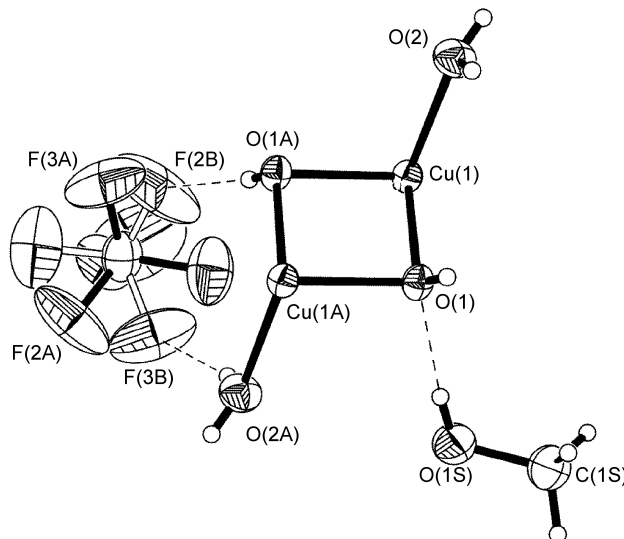


Figure 6.45: Structure of the disordered BF_4^- in $[\text{Cu}(\text{Mes-dpa})(\mu\text{-OH})(\text{H}_2\text{O})_2][\text{BF}_4]_2$ showing interaction with bridging hydroxide and terminal water ligands. Thermal ellipsoids are shown at the 20% level. Adapted from J. J. Allen, C. E. Hamilton, and A. R. Barron, *Dalton Trans.*, 2010, 11451.

An example that does adhere to global symmetry elements is seen in the BF_4^- anion of $[\text{Cu}\{2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{quin})_2\}_2][\text{BF}_4]\cdot\text{MeOH}$ (Figure 6.46), which exhibits a hydrogen-bonding interaction with a disordered methanol solvent molecule. The structure of R-N(quin) $_2$ is shown in Figure 6.39b. By crystallographic symmetry, the carbon atom from methanol and the boron atom from the BF_4^- anion lie on a C_2 -axis. Fluorine atoms [F(1)-F(4)], the methanol oxygen atom, and the hydrogen atoms attached to methanol O(1S) and C(1S) atoms were refined as having 50:50 site occupancy disorder (Figure 6.46).

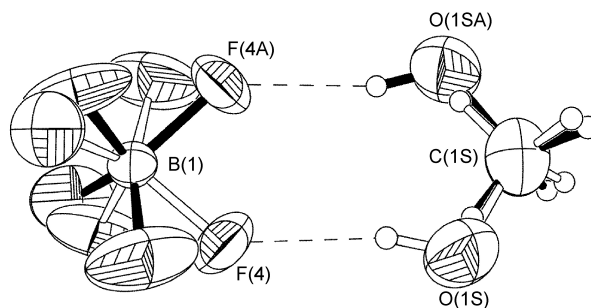


Figure 6.46: H-bonding interaction in $[\text{Cu}\{2,6\text{-}^1\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{quin})_2\}_2]\text{BF}_4\cdot\text{MeOH}$ between anion and solvent of crystallization, both disordered about a crystallographic C_2 -rotation axis running through the $\text{B}(1)\cdots\text{C}(1\text{S})$ vector. Adapted from J. J. Allen, C. E. Hamilton, and A. R. Barron, *Dalton Trans.*, 2010, 11451.

6.3.2.3.4 Non crystallographic inversion center at the boron atom

Multiple disorders can be observed with a single crystal unit cell. For example, the two BF_4^- anions in $[\text{Cu}(\text{Mes-dpa})(\text{styrene})]\text{BF}_4$ both exhibited 50:50 site occupancy disorders, the first is a C_2 -rotation tilted off one of the B-F bonds, while the second is disordered about an inversion centered on the boron atom. Refinement of the latter was carried out similarly to the aforementioned cases, with the exception that fixed distance restraints for non-bonded atoms (DANG) were left in place for the disordered fluorine atoms attached to B(2) (Figure 6.47).

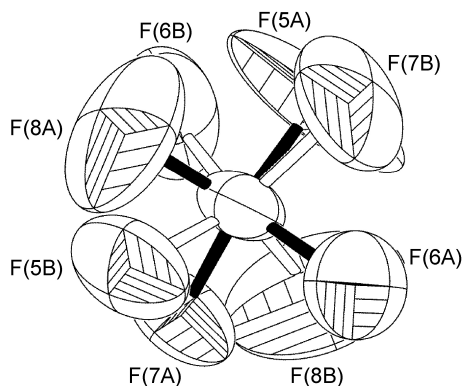


Figure 6.47: Structure for the disordered BF_4^- anion due to a NCS-inversion center, in compound $[\text{Cu}(\text{Mes-dpa})(\text{styrene})]\text{BF}_4$ with both parts of the disorders present. Thermal ellipsoids are shown at the 20% level. Adapted from J. J. Allen, C. E. Hamilton, and A. R. Barron, *Dalton Trans.*, 2010, 11451.

6.3.2.3.5 Disorder on a crystallographic mirror plane

Another instance in which the BF_4^- anion is disordered about a crystallographic symmetry element is that of $[\text{Cu}(\text{H-dpa})(1,5\text{-cyclooctadiene})]\text{BF}_4$. In this instance fluorine atoms F(1) through F(4) are present in the asymmetric unit of the complex. Disordered atoms F(1A)-F(4A) were refined with 50% site occupancies, as B(1) lies on a mirror plane (Figure 6.48). For initial refinement cycles, similar distance restraints (SADI) were placed on all B-F and F-F distances, in addition to similar ADP restraints (SIMU) and rigid bond restraints (DELU) for all F atoms. Restraints were lifted for final refinement cycles, in which the boron atom lies on a crystallographic mirror plane, and all four fluorine atoms are reflected across.

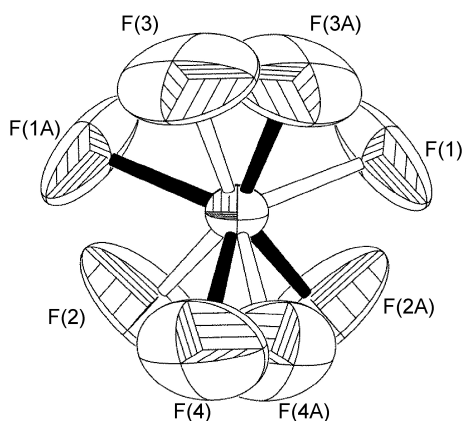


Figure 6.48: Molecular structure for the anion in $[\text{Cu}(\text{H-dpa})(1,5\text{-cyclooctadiene})]\text{BF}_4$ with both parts of the disordered BF_4^- present. For clarity, thermal ellipsoids are shown at the 20% level. Adapted from J. J. Allen and A. R. Barron, *Dalton Trans.*, 2009, 878.

6.3.2.3.6 Disorder on a non-crystallographic mirror plane

It has been observed that the BF_4^- anion can exhibit site occupancy disorder of the boron atom and one of the fluorine atoms across an NCS mirror plane defined by the plane of the other three fluorine atoms (Figure 6.49) modeling the entire anion as disordered (including the boron atom).

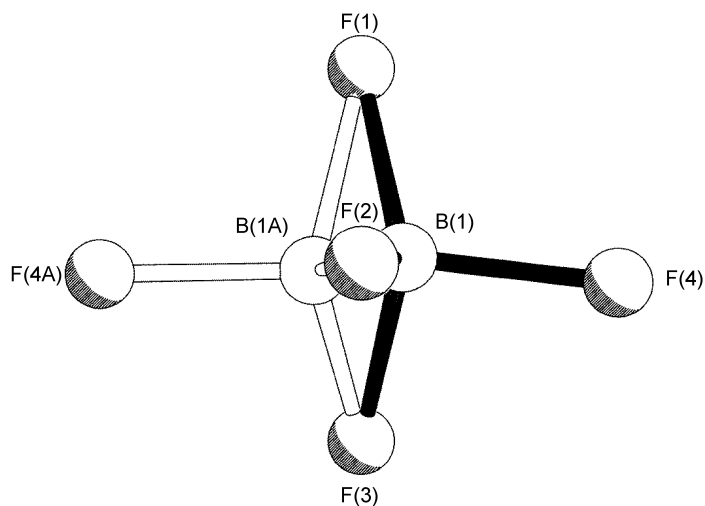


Figure 6.49: Disordered anion across the plane of three fluorine atoms. Adapted from J. T. Mague and S. W. Hawbaker, *J. Chem. Cryst.*, 1997, **27**, 603.

6.3.2.3.7 Disorder of the boron atom core

The extreme case of a disorder involves refinement of the entire anion, with all boron and all fluorine atoms occupying more than two sites (Figure 6.50). In fact, some disorders of the latter types must be refined isotropically, or as a last-resort, not at all, to prevent one or more atoms from turning non-positive definite.

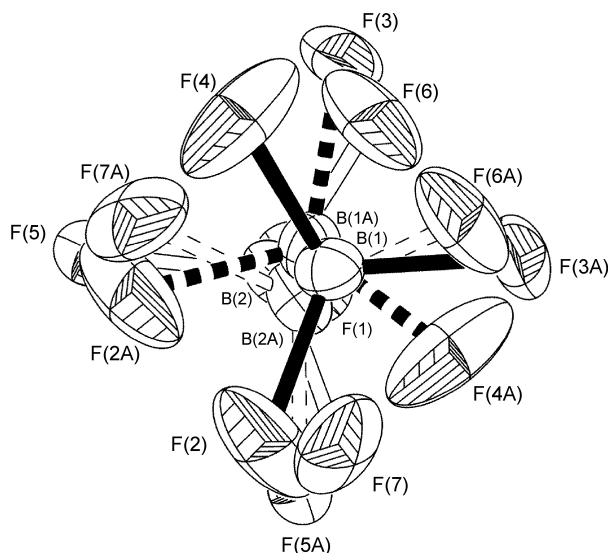


Figure 6.50: An example of a structure of a highly disordered BF_4^- anion refined with four site occupancies for all boron and fluorine atoms. Adapted from P. Szklarz, M. Owczarek, G. Bator, T. Lis, K. Gatner, and R. Jakubas, *J. Mol. Struct.*, 2009, **929**, 48.

6.3.2.4 Bibliography

- J. J. Allen and A. R. Barron, *J. Chem. Cryst.*, 2009, **39**, 935.
- J. J. Allen and A. R. Barron, *Dalton Trans.*, 2009, 878.
- J. J. Allen, C. E. Hamilton, and A. R. Barron, *Dalton Trans.*, 2010, 11451.
- W. Clegg, *Crystal Structure Determination*, Oxford University Press, NY (1998).
- *IUCr Monographs on Crystallography*, Ed. E. Domenicano and I. Hargittai, Oxford University Press, NY, (1992).
- *Crystallographic Computing 6: A Window on Modern Crystallography*, Ed. H. D. Flack, L. Parkanyi, and K. Simon, Oxford University Press, NY (1993).
- F. L. Hirshfield, *Acta Cryst.*, 1976, **A32**, 239.
- J. T. Mague and S. W. Hawbaker, *J. Chem. Cryst.*, 1997, **27**, 603.
- S. Martinez-Vargas, R. Toscano, and J. Valdez-Martinez, *Acta Cryst.*, 2007, **E63**, m1975.
- P. Müller, *Crystal Structure Refinement, A Crystallographer's Guide to SHELXL*, Oxford University Press, UK (2006).
- D. F. Mullica, S. L. Gibson, E. L. Sappenfield, C. C. Lin, and D. H. Leschnitzer, *Inorg. Chim. Acta*, 1990, **177**, 89.
- P. Szklarz, M. Owczarek, G. Bator, T. Lis, K. Gatner, and R. Jakubas, *J. Mol. Struct.*, 2009, **929**, 48.

6.4 Neutron Diffraction ⁵

6.4.1 Introduction

The first neutron diffraction experiment was in 1945 by Ernest O. Wollan (Figure 6.51) using the Graphite Reactor at Oak Ridge. Along with Clifford Shull (Figure 6.51) they outlined the principles of the technique. However, the concept that neutrons would diffract like X-rays was first proposed by Dana Mitchell and Philip Powers. They proposed that neutrons have a wave like structure, which is explained by the de Broglie equation, (6.11), where λ is the wavelength of the source usually measured in Å, h is Planck's constant, v is the velocity of the neutron, and finally m represents the mass of the neutron.

$$\lambda = h/mv \quad (6.11)$$



Figure 6.51: American physicists Ernest Wollan (1902 - 1984) and (standing) Clifford Shull (1915 – 2001).

The great majority of materials that are studied by diffraction methods are composed of crystals. X-rays where the first type of source tested with crystals in order to determine their structural characteristics. Crystals are said to be perfect structures although some of them show defects on their structure. Crystals are composed of atoms, ions or molecules, which are arranged, in a uniform repeating pattern. The basic concept to understand about crystals is that they are composed of an array of points, which are called lattice points, and the motif, which represents the body part of the crystal. Crystals are composed of a series of unit cells. A unit cell is the repeating portion of the crystal. Usually there are another eight unit cells surrounding each unit cell. Unit cells can be categorized as primitive, which have only one lattice point. This means that the unit cell will only have lattice points on the corners of the cell. This point is going to be shared with eight other unit cells. Whereas in a non primitive cell there will also be point in the corners of the cell but in addition there will be lattice points in the faces or the interior of the cell, which similarly will be shared by other cells. The only primitive cell known is the simple crystal system and for nonprimitive cells there are known face-centered cubic, base centered cubic and body centered cubic.

⁵This content is available online at <<http://cnx.org/content/m43582/1.1/>>.

Crystals can be categorized depending on the arrangement of lattice points; this will generate different types of shapes. There are known seven crystal systems, which are cubic, tetragonal, orthorhombic, rhombohedral, hexagonal, monoclinic and triclinic. All of these have different angles and the axes are equally the same or different in others. Each of these type of systems have different bravais lattice.

6.4.1.1 Braggs law

Braggs Law was first derived by physicist Sir W.H. Bragg (Figure 6.52) and his son W. L Bragg (Figure 6.53) in 1913.

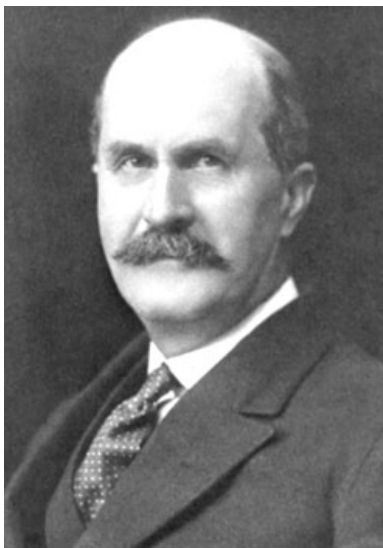


Figure 6.52: British physicist, chemist, mathematician and active sportsman Sir William H. Bragg (1862 - 1942).

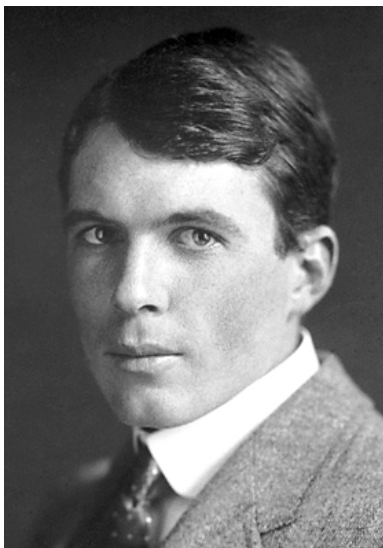


Figure 6.53: Australian-born British physicist William L. Bragg (1890 - 1971).

It has been used to determine the spacing of planes and angles formed between these planes and the incident beam that had been applied to the crystal examined. Intense scattered X-rays are produced when X-rays with a set wavelength are executed to a crystal. These scattered X-rays will interfere constructively due the equality in the differences between the travel path and the integral number of the wavelength. Since crystals have repeating units patterns, diffraction can be seen in terms of reflection from the planes of the crystals. The incident beam, the diffracted beam and normal plane to diffraction need to lie in the same geometric plane. The angle, which the incident beam forms when it hits the plane of the crystal, is called 2θ . Figure 6.54 shows a schematic representation of how the incident beam hits the plane of the crystal and is reflected at the same angle 2θ , which the incident beam hits. Bragg's Law is mathematically expressed, (6.12), where, n = integer order of reflection, λ = wavelength, d = plane spacing.

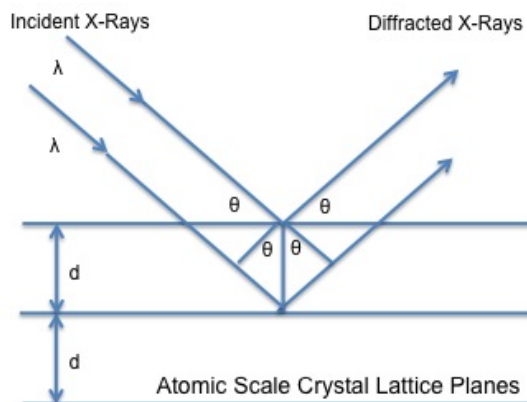


Figure 6.54: Bragg's Law construction.

$$n\lambda = 2d \sin\theta \quad (6.12)$$

Bragg's Law is essential in determining the structure of an unknown crystal. Usually the wavelength is known and the angle of the incident beam can be measured. Having these two known values, the plane spacing of the layer of atoms or ions can be obtained. All reflections collected can be used to determine the structure of the unknown crystal material.

Bragg's Law applies similarly to neutron diffraction. The same relationship is used the only difference being is that instead of using X-rays as the source, neutrons that are ejected and hit the crystal are being examined.

6.4.1.2 Neutron diffraction

Neutrons have been studied for the determination of crystalline structures. The study of materials by neutron radiation has many advantages against the normally used such as X-rays and electrons. Neutrons are scattered by the nucleus of the atoms rather than X-rays, which are scattered by the electrons of the atoms. These generates several differences between them such as that scattering of X-rays highly depend on the atomic number of the atoms whereas neutrons depend on the properties of the nucleus. These lead to a greater and accurately identification of the unknown sample examined if neutron source is being used. The nucleus of every atom and even from isotopes of the same element is completely different. They all have different characteristics, which make neutron diffraction a great technique for identification of materials, which have similar elemental composition. In contrast, X-rays will not give an exact solution if similar characteristics are known between materials. Since the diffraction will be similar for adjacent atoms further analysis needs to be done in order to determine the structure of the unknown. Also, if the sample contains light elements such as hydrogen, it is almost impossible to determine the exact location of each of them just by X-ray diffraction or any other technique. Neutron diffraction can tell the number of light elements and the exact position of them present in the structure.

6.4.1.2.1 Neutron inventors

Neutrons were first discovered by James Chadwick in 1932 Figure 6.55 when he showed that there were uncharged particles in the radiation he was using. These particles had a similar mass of the protons but did not have the same characteristics as them. Chadwick followed some of the predictions of Rutherford who

first worked in this unknown field. Later, Elsasser designed the first neutron diffraction in 1936 and the ones responsible for the actual constructing were Halban and Preiswerk. This was first constructed for powders but later Mitchell and Powers developed and demonstrated the single crystal system. All experiments realized in early years were developed using radium and beryllium sources. The neutron flux from these was not sufficient for the characterization of materials. Then, years passed and neutron reactors had to be constructed in order to increase the flux of neutrons to be able to realize a complete characterization the material being examined.

Between mid and late 40s neutron sources began to appear in countries such as Canada, UK and some other of Europe. Later in 1951 Shull and Wollan (Figure 6.51) presented a paper that discussed the scattering lengths of 60 elements and isotopes, which generated a broad opening of neutron diffraction for the structural information that can be obtained from neutron diffraction.



Figure 6.55: English Nobel laureate in physics James Chadwick (1891-1974)

6.4.2 Neutron sources

The first source of neutrons for early experiments was gathered from radium and beryllium sources. The problem with this, as already mentioned, was that the flux was not enough to perform huge experiments such as the determination of the structure of an unknown material. Nuclear reactors started to emerge in early 50s and these had a great impact in the scientific field. In the 1960s neutron reactors were constructed depending on the desired flux required for the production of neutron beams. In USA the first one constructed was the High Flux Beam Reactor (HFBR). Later, this was followed by one at Oak Ridge Laboratory (HFIR) (Figure 6.56), which also was intended for isotope production and a couple of years later the ILL was built. This last one is the most powerful so far and it was built by collaboration between Germany and France. These nuclear reactors greatly increased the flux and so far there has not been constructed any other better reactor. It has been discussed that probably the best solution to look for greater flux is to look for other approaches for the production of neutrons such as accelerator driven sources. These could greatly increase the flux of neutrons and in addition other possible experiments could be executed. The key point in these devices is spallation, which increases the number of neutrons executed from a single proton and the energy released

is minimal. Currently, there are several of these around the world but investigations continue searching for the best approach of the ejection of neutrons.

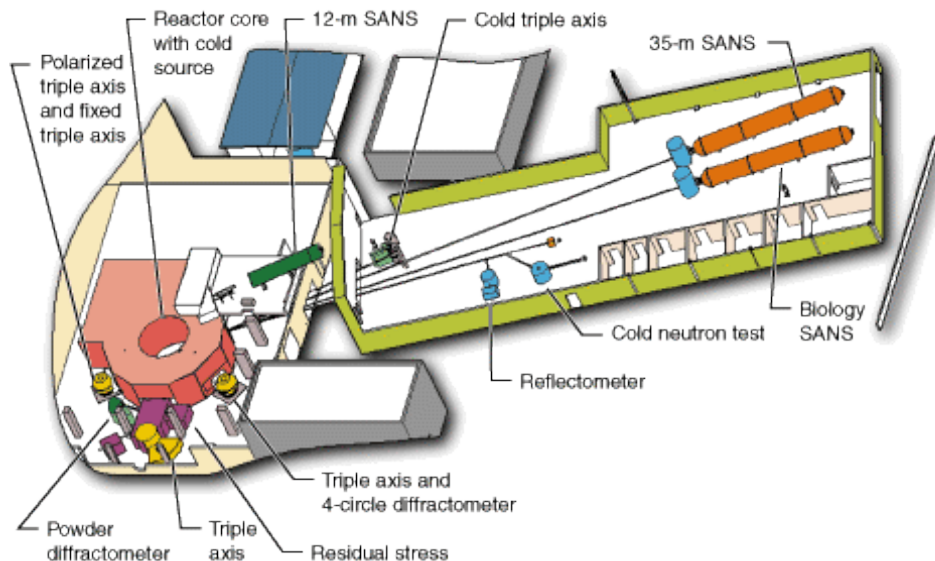
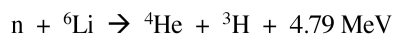
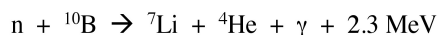
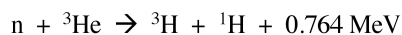


Figure 6.56: Schematic representation of HIFR. Courtesy of Oak Ridge National Laboratory, US Dept. of Energy

6.4.3 Neutron detectors

Although neutrons are great particles for determining complete structures of materials they have some disadvantages. These particles experiment a reasonably weak scattering when looking especially to soft materials. This is a huge concern because there can be problems associated with the scattering of the particles which can lead to a misunderstanding in the analysis of the structure of the material.

Neutrons are particles that have the ability to penetrate through the surface of the material being examined. This is primarily due to the nuclear interaction produced from the particles and the nucleus from the material. This interaction is much greater than the one performed from the electrons, which it is only an electrostatic interaction. Also, it cannot be omitted the interaction that occurs between the electrons and the magnetic moment of the neutrons. All of these interactions discussed are of great advantage for the determination of the structure since neutrons interact with every single nucleus in the material. The problem comes when the material is being analyzed because neutrons being uncharged materials make them difficult to detect them. For this reason, neutrons need to be reacted in order to generate charged particles, ions. Some of the reactions usually used for the detection of neutrons are:



The first two reactions apply when the detection is performed in a gas environment whereas the third one is carried out in a solid. In each of these reaction there is a large cross section, which makes them ideal

for neutron capture. The neutron detection hugely depends on the velocity of the particles. As velocity increases, shorter wavelengths are produced and the less efficient the detection becomes. The particles that are executed to the material need to be as close as possible in order to have an accurate signal from the detector. These signal needs to be quickly transduced and the detector should be ready to take the next measurement.

In gas detectors the cylinder is filled up with either ^3He or BF_3 . The electrons produced by the secondary ionization interact with the positively charged anode wire. One disadvantage of this detector is that it cannot be attained a desired thickness since it is very difficult to have a fixed thickness with a gas. In contrast, in scintillator detectors since detection is developed in a solid, any thickness can be obtained. The thinner the thickness of the solid the more efficient the results obtained become. Usually the absorber is ^6Li and the substrate, which detects the products, is phosphor, which exhibits luminescence. This emission of light produced from the phosphor results from the excitation of this when the ions pass thorough the scintillator. Then the signal produced is collected and transduced to an electrical signal in order to tell that a neutron has been detected.

6.4.4 Neutron scattering

One of the greatest features of neutron scattering is that neutrons are scattered by every single atomic nucleus in the material whereas in X-ray studies, these are scattered by the electron density. In addition, neutron can be scattered by the magnetic moment of the atoms. The intensity of the scattered neutrons will be due to the wavelength at which it is executed from the source. Figure 6.57 shows how a neutron is scattered by the target when the incident beam hits it.

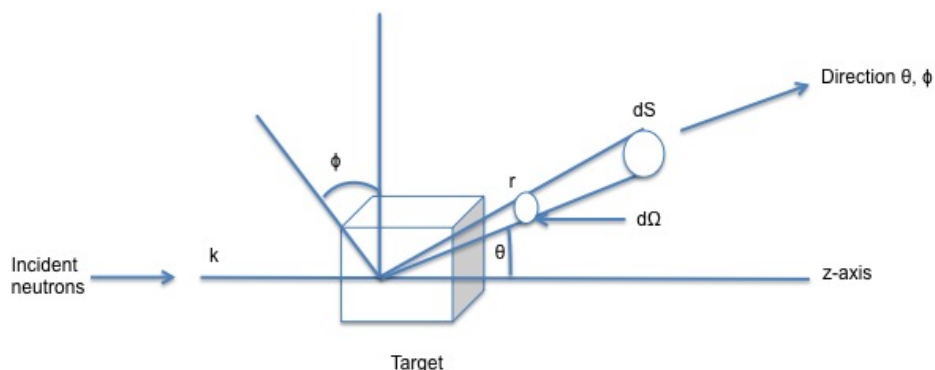


Figure 6.57: Schematic representation of scattering of neutrons when it hits the target. Adapted from W. Marshall and S. W. Lovesey, *Theory of thermal neutron scattering: the use of neutrons for the investigation of condensed matter*, Clarendon Press, Oxford (1971).

The incident beam encounters the target and the scattered wave produced from the collision is detected by a detector at a defined position given by the angles θ , ϕ which are joined by the $d\Omega$. In this scenario there is assumed that there is no transferred energy between the nucleus of the atoms and the neutron ejected, leads to an elastic scattering.

When there is an interest in calculating the diffracted intensities the cross sectional area needs to be separated into scattering and absorption respectively. In relation to the energies of these there is moderately large range for constant scattering cross section. Also, there is a wide range cross sections close to the nuclear resonance. When the energies applied are less than the resonance the scattering length and scattering cross

section are moved to the negative side depending on the structure being examined. This means that there is a shift on the scattering, therefore the scattering will not be in a 180° phase. When the energies are higher than resonance it means that the cross section will be asymptotic to the nucleus area. This will be expected for spherical structures. There is also resonance scattering when there are different isotopes because each produce different nuclear energy levels.

6.4.4.1 Coherent and incoherent scattering

Usually in every material, atoms will be arranged differently. Therefore, neutrons when scattered will be either coherently or incoherently. It is convenient to determine the differential scattering cross section, which is given by (6.13), where b represents the mean scattering length of the atoms, k is the scattering vector, r_n is the position of the vector of the analyzed atom and lastly N is the total number of atoms in the structure. This equation can be separated in two parts, which one corresponds to the coherent scattering and the incoherent scattering as labeled below. Usually the particles scattered will be coherent which facilitates the solution of the cross section but when there is a difference in the mean scattering length, there will be a complete arrangement of the formula and these new changes (incoherent scattering) should be considered. Incoherent scattering is usually due to the isotopes and nuclear spins of the atoms in the structure.

$$\frac{d\sigma}{d\Omega} = \underbrace{|b|^2 |\sum \exp(ik \cdot r_n)|^2}_{\text{coherent}} + \underbrace{N|b-b|^2}_{\text{incoherent}} \quad (6.13)$$

The ability to distinguish atoms with similar atomic number or isotopes is proportional to the square of their corresponding scattering lengths. There are already known several coherent scattering lengths of some atoms which are very similar to each other. Therefore, it makes even easier to identify by neutrons the structure of a sample. Also neutrons can find ions of light elements because they can locate very low atomic number elements such as hydrogen. Due to the negative scattering that hydrogen develops it increases the contrast leading to a better identification of it, although it has a very large incoherent scattering which causes electrons to be removed from the incident beam applied.

6.4.4.2 Magnetic scattering

As previously mentioned one of the greatest features about neutron diffraction is that neutrons because of their magnetic moment can interact with either the orbital or the spin magnetic moment of the material examined. Not all every single element in the periodic table can exhibit a magnetic moment. The only elements that show a magnetic moment are those, which have unpaired electrons spins. When neutrons hit the solid this produces a scattering from the magnetic moment vector as well as the scattering vector from the neutron itself. Below Figure 6.58 shows the different vectors produced when the incident beam hits the solid.

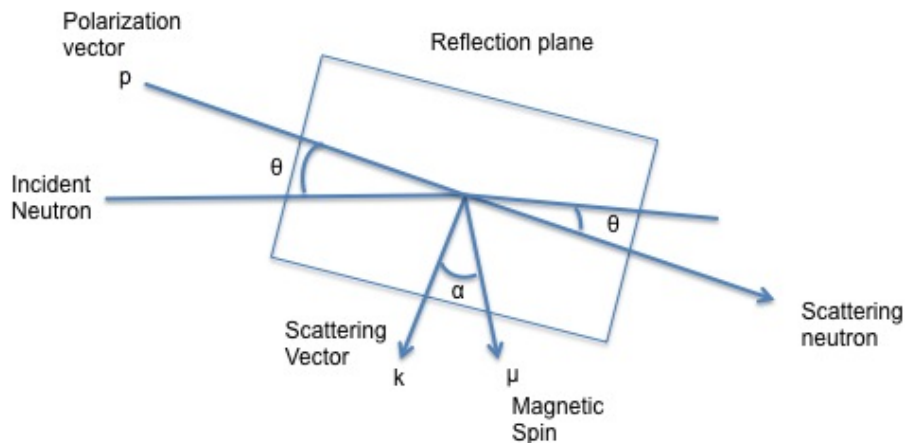


Figure 6.58: Diagram of magnetic Scattering of neutrons. Adapted from G. E. Bacon, *Neutron Diffraction*, Clarendon Press, Oxford (1975).

When looking at magnetic scattering it needs to be considered the coherent magnetic diffraction peaks where the magnetic contribution to the differential cross section is p^2q^2 for an unpolarized incident beam. Therefore the magnetic structure amplitude will be given by (6.13), where q_n is the magnetic interaction vector, p_n is the magnetic scattering length and the rest of the terms are used to know the position of the atoms in the unit cell. When this term F_{mag} is squared, the result is the intensity of magnetic contribution from the peak analyzed. This equation only applies to those elements which have atoms that develop a magnetic moment.

$$F_{\text{mag}} = \sum p_n q_n \exp\{2\pi i(hx_n + ky_n + lz_n)\}$$

Magnetic diffraction becomes very important due to its d-spacing dependence. Due to the greater effect produced from the electrons in magnetic scattering the forward scattering has a greater strength than the backward scattering. There can also be developed similar as in X-ray, interference between the atoms which makes structure factor also be considered. These interference effects could be produced by the wide range in difference between the electron distribution and the wavelength of the thermal neutrons. This factor quickly decreases as compared to X-rays because the beam only interacts with the outer electrons of the atoms.

6.4.5 Sample preparation and environment

In neutron diffraction there is not a unique protocol of factors that should be considered such as temperature, electric field and pressure to name a few. Depending on the type of material and data that has been looked the parameters are assigned. There can be reached very high temperatures such as 1800K or it can go as low as 4K. Usually to get to these extreme temperatures a special furnace capable of reaching these temperatures needs to be used. For example, one of the most common used is the He refrigerator when working with very low temperatures. For high temperatures, there are used furnaces with a heating element cylinder such as vanadium (V), niobium (Nb), tantalum (Ta) or tungsten (W) that is attached to copper bars which hold the sample. Figure 6.59 shows the design for the vacuum furnaces used for the analysis. The metal that works best at the desired temperature range will be the one chosen as the heating element. The metal that is commonly used is vanadium because it prevents the contribution of other factors such as coherent scattering. Although with this metal this type of scattering is almost completely reduced. Other important factor about this furnaces is that the material been examined should not decompose under vacuum conditions. The

crystal needs to be as stable as possible when it is being analyzed. When samples are not able to persist at a vacuum environment, they are heated in the presence of several gases such as nitrogen or argon.

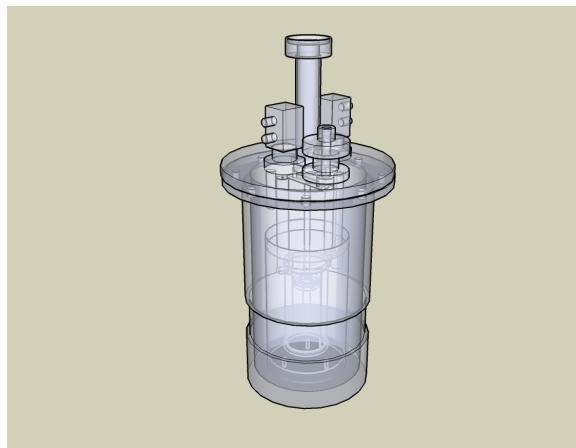


Figure 6.59: Metallic chamber which holds the sample. Courtesy of Nuclear Physics Institute.

Usually in order to prepare the samples that are being examined in neutron diffraction it is needed large crystals rather small ones as the one needed for X-ray studies. This one of the main disadvantages of this instrument. Most experiments are carried out using a four-circle diffractometer. The main reason being is because several experiment are carried out using very low temperatures and in order to achieve a good spectra it is needed the He refrigerator. First, the crystal being analyzed is mounted on a quartz slide, which needs to be a couple millimeters in size. Then, it is inserted into the sample holder, which is chosen depending on the temperatures wanted to be reached. In addition, neutrons can also analyze powder samples and in order to prepare the sample for these they need to be completely rendered into very fine powders and then inserted into the quartz slide similarly to the crystal structures. The main concern with this method is that when samples are grounded into powders the structure of the sample being examined can be altered.

6.4.6 Summary

Neutron diffraction is a great technique used for complete characterization of molecules involving light elements and also very useful for the ones that have different isotopes in the structure. Due to the fact that neutrons interact with the nucleus of the atoms rather than with the outer electrons of the atoms such as X-rays, it leads to a more reliable data. In addition, due to the magnetic properties of the neutrons there can be characterized magnetic compounds due to the magnetic moment that neutrons develop. There are several disadvantages as well, one of the most critical is that there needs to be a good amount of sample in order to be analyzed by this technique. Also, great amounts of energy are needed to produce large amounts of neutrons. There are several powerful neutron sources that have been developed in order to conduct studies of largest molecules and a smaller quantity of sample. However, there is still the need of devices which can produce a great amount of flux to analyze more sophisticated samples. Neutron diffraction has been widely studied due to the fact that it works together with X-rays studies for the characterization of crystalline samples. The properties and advantages of this technique can greatly increased if some of the disadvantages are solved. For example, the study of molecules which exhibit some type of molecular force can be characterized. This will be because neutrons can precisely locate hydrogen atoms in a sample. Neutrons have gives a better

answer to the chemical interactions that are present in every single molecule, whereas X-rays help to give an idea of the macromolecular structure of the samples being examined.

6.4.7 Bibliography

- G. E. Bacon, *Neutron Diffraction*, Clarendon Press, Oxford (1975).
- R. K. Crawford, *SPIE*, 1992, **1737**, 210.
- B. D. Cullity, *Elements of X-Ray Diffraction*, 3rd Edition, Prentice Hall, New Jersey (2001).
- W. Marshall and S. W. Lovesey, *Theory of thermal neutron scattering: the use of neutrons for the investigation of condensed matter*, Clarendon Press, Oxford (1971).
- D. P. Mitchel and P. N. Powers, *Phys. Rev.*, 1936, **50**, 486.
- C. G. Shull and E. O. Wollan, *Phys. Rev.*, 1951, **81**, 527.

6.5 XAFS

6.5.1 XAFS Analysis for Arsenic Adsorption onto Iron Oxides⁶

6.5.1.1 Introduction

X-ray absorption fine structure (XAFS) spectroscopy includes both X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopies. The difference between both techniques is the area to analyze, as shown Figure 6.60 and the information each technique provides. The complete XAFS spectrum is collected across an energy range of around 200 eV before the absorption edge of interest and until 1000 eV after it (Figure 6.60). The absorption edge is defined as the X-ray energy when the absorption coefficient has a pronounced increasing. This energy is equal to the energy required to excite an electron to an unoccupied orbital.

⁶This content is available online at <<http://cnx.org/content/m38287/1.2/>>.

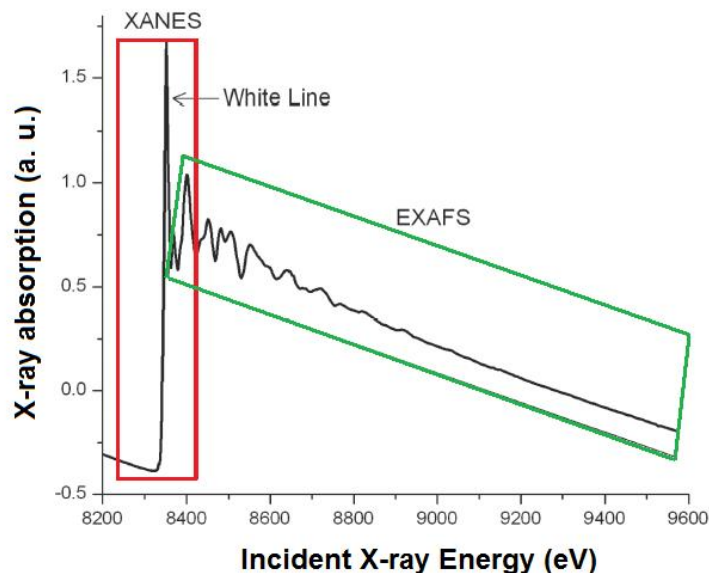


Figure 6.60: Characteristic spectra areas for X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopies. Adapted from S. D. Kelly, D. Hesterberg, and B. Ravel in *Methods of Soil Analysis: Part 5, Mineralogical Methods*, Ed. A. L. Urely and R. Drees, Soil Science Society of America Book Series, Madison (2008).

X-ray absorption near edge structure (XANES) is used to determine the valence state and coordination geometry, whereas extended X-ray absorption fine structure (EXAFS) is used to determine the local molecular structure of a particular element in a sample.

6.5.1.1.1 X-ray absorption near edge structure (XANES) spectra

XANES is the part of the absorption spectrum closer an absorption edge. It covers from approximately -50 eV to +200 eV relative to the edge energy (Figure 6.60). Because the shape of the absorption edge is related to the density of states available for the excitation of the photoelectron, the binding geometry and the oxidation state of the atom affect the XANES part of the absorption spectrum.

Before the absorption edge, there is a linear and smooth area. Then, the edge appears as a step, which can have other extra shapes as isolated peaks, shoulders or a *white line*, which is a strong peak onto the edge. Those shapes give some information about the atom. For example, the presence of a white line indicates that after the electron releasing, the atomic states of the element is confined by the potential it feels. This peak sharp would be smoothed if the atom could enter to any kind of resonance. Important information is given because of the absorption edge position. Atoms with higher oxidation state have fewer electrons than protons, so, the energy states of the remaining electrons are lowered slightly, which causes a shift of the absorption edge energy up to several eV to a higher X-ray energy.

6.5.1.1.2 Extended X-ray absorption fine structure (EXAFS) spectra

The EXAFS part of the spectrum is the oscillatory part of the absorption coefficient above around 1000 eV of the absorption edge. This region is used to determine the molecular bonding environments of the elements. EXAFS gives information about the types and numbers of atoms in coordination a specific atom and their

inter-atomic distances. The atoms at the same radial distance from a determinate atom form a shell. The number of the atoms in the shell is the coordination number (e.g., Figure 6.61).

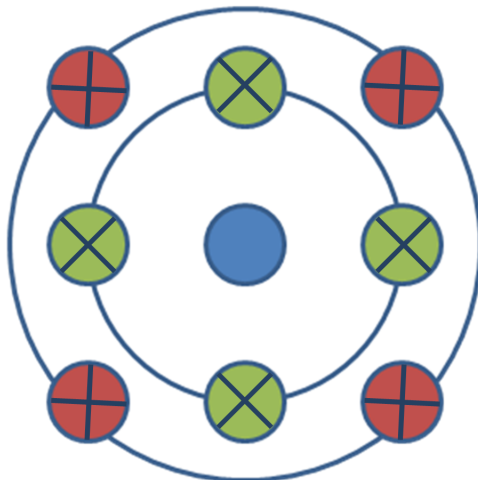


Figure 6.61: A schematic representation of coordination number in different layers in which there are two shells around the center atom. Both shells, green (x) and red (+), have coordination numbers of 4, but the radial distance of the red one (+) is bigger than the green one (x). Based on S. D. Kelly, D. Hesterberg, and B. Ravel in *Methods of Soil Analysis: Part 5, Mineralogical Methods*, Ed. A. L. Urely and R. Drees, Soil Science Society of America Book Series, Madison (2008).

An EXAFS signal is given by the photoelectron scattering generated for the center atom. The phase of the signal is determinate by the distance and the path the photoelectrons travel. A simple scheme of the different paths is shown by Figure 6.62. In the case of two shells around the centered atom, there is a degeneracy of four for the path between the main atom to the first shell, a degeneracy of four for the path between the main atom to the second shell, and a degeneracy of eight for the path between the main atom to the first shell, to the second one and to the center atom.

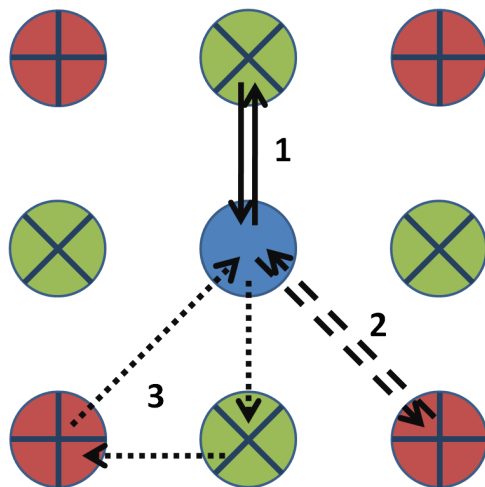


Figure 6.62: A two shell diagram in which there are three kinds of paths. From the center atom to the green one (x) and then going back (1); from the center atom to the red one (+) and the going back (2); and from the center atom to the first shell to the second one, and the returning to the center atom (3). Based on S. D. Kelly, D. Hesterberg, and B. Ravel in *Methods of Soil Analysis: Part 5, Mineralogical Methods*, Ed. A. L. Urely and R. Drees, Soil Science Society of America Book Series, Madison (2008).

The analysis of EXAFS spectra is accomplished using Fourier transformation to fit the data to the EXAFS equation. The EXAFS equation is a sum of the contribution from all scattering paths of the photoelectrons (6.14), where each path is given by (6.15).

$$\chi(k) = \sum_i \chi_i(k) \quad (6.14)$$

$$\chi_i(k) \equiv \frac{(N_i S_0^2) F_{\text{eff}i}(k)}{k R_i^2} \sin[2kR_i + \phi_i(k)] e^{-2\sigma_i^2 k^2} e^{\frac{-2R_i}{\lambda(k)}} \quad (6.15)$$

The terms $F_{\text{eff}i}(k)$, $\phi_i(k)$, and $\lambda_i(k)$ are the effective scattering amplitude of the photoelectron, the phase shift of the photoelectron, and the mean free path of the photoelectron, respectively. The term R_i is the half path length of the photoelectron (the distance between the centered atom and a coordinating atom for a single-scattering event). And the k^2 is given by the (6.16). The remaining variables are frequently determined by modeling the EXAFS spectrum.

$$k^2 = \frac{2m_e(E - E_0 + \Delta E_0)}{\hbar} \quad (6.16)$$

6.5.1.2 XAFS analysis for arsenic adsorption onto iron oxides

The absorption of arsenic species onto iron oxide offers an example of the information that can be obtained by EXAFS. Because the huge impact that the presence of arsenic in water can produce in societies there is a lot of research in the adsorption of arsenic in several kinds of materials, in particular nano materials. Some of the materials more promising for this kind of applications are iron oxides. The elucidation of the

mechanism of arsenic coordination onto the surfaces of those materials has been studied lately using X-ray absorption spectroscopy.

There are several ways how arsenate (AsO_4^{3-} , Figure 6.63) can be adsorbed onto the surfaces. Figure 6.64 shows the three ways that Sherman proposes arsenate can be adsorbed onto goethite ($\alpha\text{-FeOOH}$): bidentate cornersharing (2C), bidentate edge sharing (2E) and monodentate corner-sharing (1V) shapes. Figure 6.65 shows that the bidentate corner sharing (2C) is the configuration that corresponds with the calculated parameters not only for goethite, but for several iron oxides.

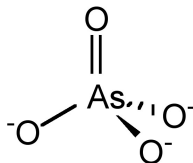


Figure 6.63: Structure of the arsenate anion.

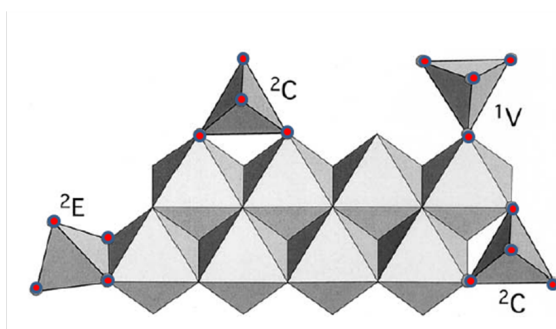


Figure 6.64: Possible configurations of arsenate onto goethite. The tetrahedral with the small spheres represents the arsenate ions. Adapted from D. M. Sherman and S. R. Randal. *Geochim. Cosmochim. Ac.* 2003, **67**, 4223.

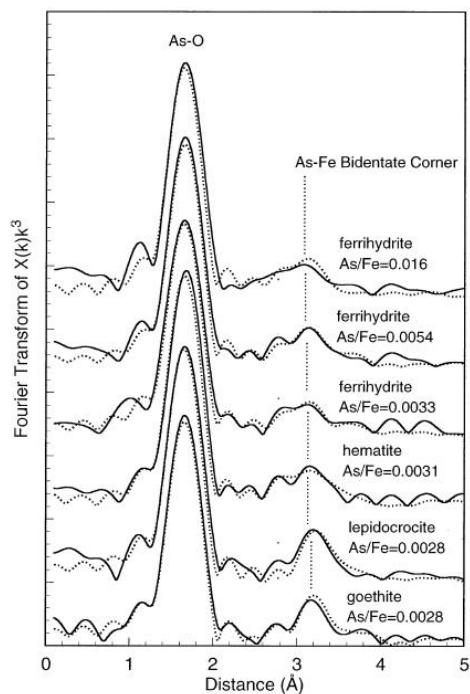


Figure 6.65: Fourier transforms of the EXAFS for arsenate sorbed onto goethite, lepidocrocite, hematite and ferrihydrite. Adapted from D. M. Sherman and S. R. Randal. *Geochim. Cosmochim. Ac.* 2003, **67**, 4223.

Several studies have confirmed that the bidentate corner sharing (2C) is the one present in the arsenate adsorption but also one similar, a tridentate corner sharing complex (3C), for the arsenite adsorption onto most of iron oxides as shows Figure 6.66. Table 6.8 shows the coordination numbers and distances reported in the literature for the As(III) and As(V) onto goethite.

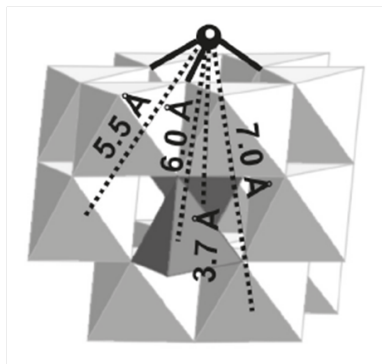


Figure 6.66: Proposed structural model for arsenic(III) tridante. Adapted from G. Morin, Y. Wang, G. Ona-Nguema, F. Juillot, G. Calas, N. Menguy, E. Aubry, J. R. Bargar, and G. E. Brown. *Langmuir* 2009, **25**, 9119.

As	CN As-O	R As-O (Å)	CN As-Fe	R As-Fe (Å)
III	3.06±0.03	1.79±0.8	2.57±0.01	3.34±3
	3.19	1.77±1	1.4	3.34±5
	3	1.78	2	3.55±5
V	1.03.0	1.631.70	2	3.30
	4.6	1.68	—	3.55±5

Table 6.8: Coordination numbers (CN) and inter-atomic distances (R) reported in the literature for the As(III) and As(V) adsorption onto goethite.

6.5.1.3 Bibliography

- G. Bunker. *Introduction to XAFS: A practical guide to X-ray Absorption Fine Structure Spectroscopy*, Cambridge University Press, Cambridge (2010).
- S. D. Kelly, D. Hesterberg, and B. Ravel in *Methods of Soil Analysis: Part 5, Mineralogical Methods*, Ed. A. L. Urely and R. Drees, Soil Science Society of America Book Series, Madison (2008).
- G. A. Waychunas, B. A. Rea, C. C. Fuller, and J. A. Davis. *Geochim. Cosmochim. Ac.* 1993, **57**, 2251.
- B. A. Manning, and S. E. Fendorf, and S. Goldberg, *Environ. Sci. Techn.*, 1998, **32**, 2383.
- D. M. Sherman and S. R. Randal, *Geochim. Cosmochim. Ac.*, 2003, **67**, 4223.
- G. Ona-Nguena, G. Morin F. Juillot, G. Calas, and G. E. Brown, *Environ. Sci. Techn.*, 2005, **39**, 9147.
- M. Stachowicz, T. Hiemstra, and W. H. Van Riemsdijk, *J. Colloid. Interf. Sci.*, 2005, **302**, 62.
- M. Auffan, J. Rose, O. Proux, D. Borschneck, A. Masion, P. Chaurand, J. L. Hazemann, C. Chaneac, J. P. Jolivet, M. R. Wiesner, A. Van Geen, and J. Y. Bottero, *Langmuir*, 2008, **24**, 3215.
- G. Ona-Nguena, G. Morin, Y. Wang, N. Menguy, F. Juillot, L. Olivi, G. Aquilanti, M. Abdelmoula, C. Ruby, J. R. Bargar, F. Guyot, G. Calas, and G. E. Brown, Jr., *Geochim. Cosmochim. Ac.*, 2009, **73**, 1359.

- G. Morin, Y. Wang, G. Ona-Nguema, F. Juillot, G. Calas, N. Menguy, E. Aubry, J. R. Bargar, and G. E. Brown Jr., *Langmuir*, 2009, **25**, 9119.
- J. Rose, M. M. Cortalezzi-Fidalgo, S. Moustier, C. Magonetto, C. D. Jones, A. R. Barron, M. R. Wiesner, and J.-Y. Bottero, *Chem. Mater.*, 2002, **14**, 621.

6.6 Circular Dichroism Spectroscopy and its Application for Determination of Secondary Structure of Optically Active Species ⁷

6.6.1 Introduction

Circular dichroism (CD) spectroscopy is one of few structure assessment methods that can be utilized as an alternative and amplification to many conventional analysis techniques with advantages such as rapid data collection and ease of use. Since most of the efforts and time spent in advancement of chemical sciences are devoted to elucidation and analysis of structure and composition of synthesized molecules or isolated natural products rather than their preparation, one should be aware of all the relevant techniques available and know which instrument can be employed as an alternative to any other technique.

The aim of this module is to introduce CD technique and discuss what kind of information one can collect using CD. Additionally, the advantages of CD compared to other analysis techniques and its limitations will be shown.

6.6.1.1 Optical activity

As CD spectroscopy can analyze only optically active species, it is convenient to start the module with a brief introduction of optical activity. In nature almost every life form is handed, meaning that there is certain degree of asymmetry, just like in our hands. One cannot superimpose right hand on the left because they are non-identical mirror images of one another. So are the chiral (handed) molecules, they exist as enantiomers, which mirror images of each other (Figure 6.67). One interesting phenomena related to chiral molecules is their ability to rotate plane of polarized light. Optical activity property is used to determine specific rotation, $[\alpha]_{\lambda}^T$, of pure enantiomer. This feature is used in polarimetry to find the *enantiomeric excess*, (ee), present in sample.

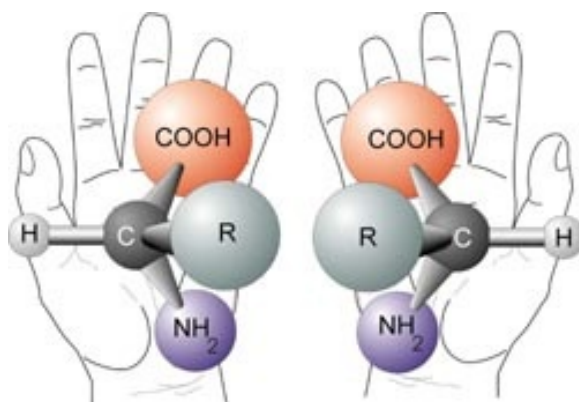


Figure 6.67: Schematic depiction of chirality/handedness of an amino acid.

⁷This content is available online at <<http://cnx.org/content/m38277/1.2/>>.

6.6.1.2 Circular dichroism

Circular dichroism (CD) spectroscopy is a powerful yet straightforward technique for examining different aspects of optically active organic and inorganic molecules. Circular dichroism has applications in variety of modern research fields ranging from biochemistry to inorganic chemistry. Such widespread use of the technique arises from its essential property of providing structural information that cannot be acquired by other means. One other laudable feature of CD is its being a quick, easy technique that makes analysis a matter of minutes. Nevertheless, just like all methods, CD has a number of limitations, which will be discussed while comparing CD to other analysis techniques.

CD spectroscopy and related techniques were considered as esoteric analysis techniques needed and accessible only to a small clandestine group of professionals. In order to make the reader more familiar with the technique, first of all, the principle of operation of CD and its several types, as well as related techniques will be shown. Afterwards, sample preparation and instrument use will be covered for protein secondary structure study case.

Depending on the light source used for generation of circularly polarized light, there are:

- Far UV CD, used to study secondary structure proteins.
- Near UV CD, used to investigate tertiary structure of proteins.
- Visible CD, used for monitoring metal ion protein interactions.

6.6.1.3 Principle of operation

In the CD spectrometer the sample is placed in a cuvette and a beam of light is passed through the sample. The light (in the present context all electromagnetic waves will be referred to as light) coming from source is subjected to circular polarization, meaning that its plane of polarization is made to rotate either clockwise (right circular polarization) or anti-clockwise (left circular polarization) with time while propagating, see Figure 6.68.

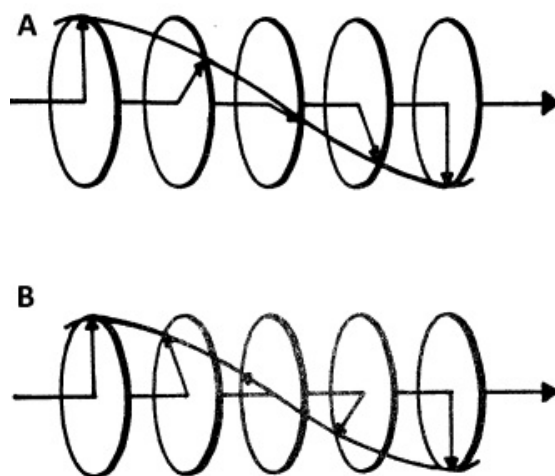


Figure 6.68: Schematic representation of (a) right circularly polarized and (b) left circularly polarized light. Adapted from L. Que, *Physical Methods in Bioinorganic Chemistry – Spectroscopy and Magnetism*, University Science Books, Sausalito (2000).

The sample is, firstly irradiated with left rotating polarized light, and the absorption is determined by (6.17). A second irradiation is performed with right polarized light. Now, due to the intrinsic asymmetry of chiral molecules, they will interact with circularly polarized light differently according to the direction of rotation there is going to be a tendency to absorb more for one of rotation directions. The difference between absorption of left and right circularly polarized light is the data, which is obtained from (6.18), where ϵ_L and ϵ_R are the molar extinction coefficients for left and right circularly polarized light, c is the molar concentration, l is the path length, the cuvette width (in cm). The difference in absorption can be related to difference in extinction, $\Delta\epsilon$, by (6.19).

$$A = \epsilon c l \quad (6.17)$$

$$\Delta A = A_L - A_R = (\epsilon_L - \epsilon_R) c l \quad (6.18)$$

$$\Delta\epsilon = \epsilon_L - \epsilon_R \quad (6.19)$$

Usually, due to historical reasons the CD is reported not only as difference in absorption or extinction coefficients but as degree of ellipticity, $[\theta]$. The relationship between $[\theta]$ and $\Delta\epsilon$ is given by (6.20).

$$[\theta] = 3,298 \Delta\epsilon \quad (6.20)$$

Since the absorption is monitored in a range of wavelengths, the output is a plot of $[\theta]$ versus wavelength or $\Delta\epsilon$ versus wavelength. Figure 6.69 shows the CD spectrum of Δ -[Co(en)₃]Cl₃.

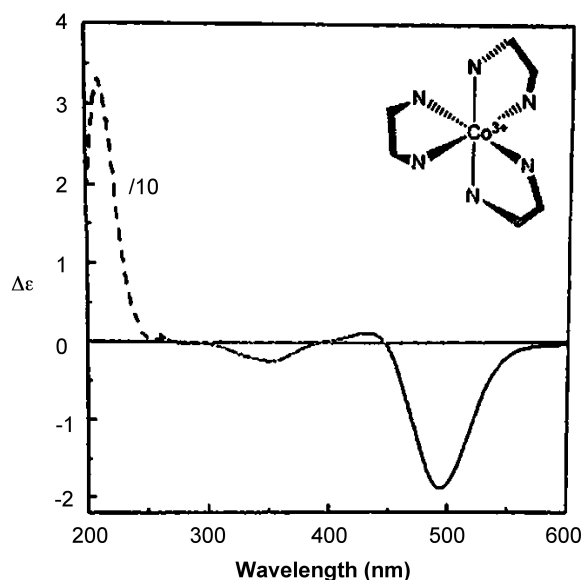


Figure 6.69: CD spectrum of Δ -[Co(en)₃]Cl₃.

6.6.2 Related techniques

6.6.2.1 Magnetic circular dichroism

Magnetic circular dichroism (MCD) is a sister technique to CD, but there are several distinctions:

- MCD does not require the sample to possess intrinsic asymmetry (i.e., chirality/optical activity), because optical activity is induced by applying magnetic field parallel to light.
- MCD and CD have different selection rules, thus information obtained from these two sister techniques is different. CD is good for assessing environment of the samples' absorbing part while MCD is superior for obtaining detailed information about electronic structure of absorbing part.

MCD is powerful method for studying magnetic properties of materials and has recently been employed for analysis of iron-nitrogen compound, the strongest magnet known. Moreover, MCD and its variation, variable temperature MCD are complementary techniques to Mossbauer spectroscopy and electron paramagnetic resonance (EPR) spectroscopy. Hence, these techniques can give useful amplification to the chapter about Mossbauer and EPR spectroscopy.

6.6.2.2 Linear dichroism

Linear dichroism (LD) is also a very closely related technique to CD in which the difference between absorbance of perpendicularly and parallelly polarized light is measured. In this technique the plane of polarization of light does not rotate. LD is used to determine the orientation of absorbing parts in space.

6.6.3 Advantages and limitations of CD

Just like any other instrument CD has its strengths and limits. The comparison between CD and NMR shown in Table 6.9 gives a good sense of capabilities of CD.

CD	NMR
Molecules of any size can be studied	There is size limitation
The experiments are quick to perform; single wavelength measurements require milliseconds.	This is not the case all of the time.
Unique sensitivity to asymmetry in sample's structure.	Special conditions are required to differentiate between enantiomers.
Can work with very small concentrations, by lengthening the cuvette width until discernable absorption is achieved.	There is a limit to sensitivity of instrument.
Timescale is much shorter (UV) thus allowing to study dynamic systems and kinetics.	Timescale is long, use of radio waves gives average of all dynamic systems.
Only qualitative analysis of data is possible.	Quantitative data analysis can be performed to estimate chemical composition.
<i>continued on next page</i>	

Does not provide atomic level structure analysis	Very powerful for atomic level analysis, providing essential information about chemical bonds in system.
The observed spectrum is not enough for claiming one and only possible structure	The NMR spectrum is key information for assigning a unique structure.

Table 6.9: A comparison of CD spectroscopy to NMR spectroscopy.

6.6.4 What kind of data is obtained from CD?

One effective way to demonstrate capabilities of CD spectroscopy is to cover the protein secondary structure study case, since CD spectroscopy is well-established technique for elucidation of secondary structure of proteins as well as any other macromolecules. By using CD one can estimate the degree of conformational order (what percent of the sample proteins is in α -helix and/or β -sheet conformation), see Figure 6.70.

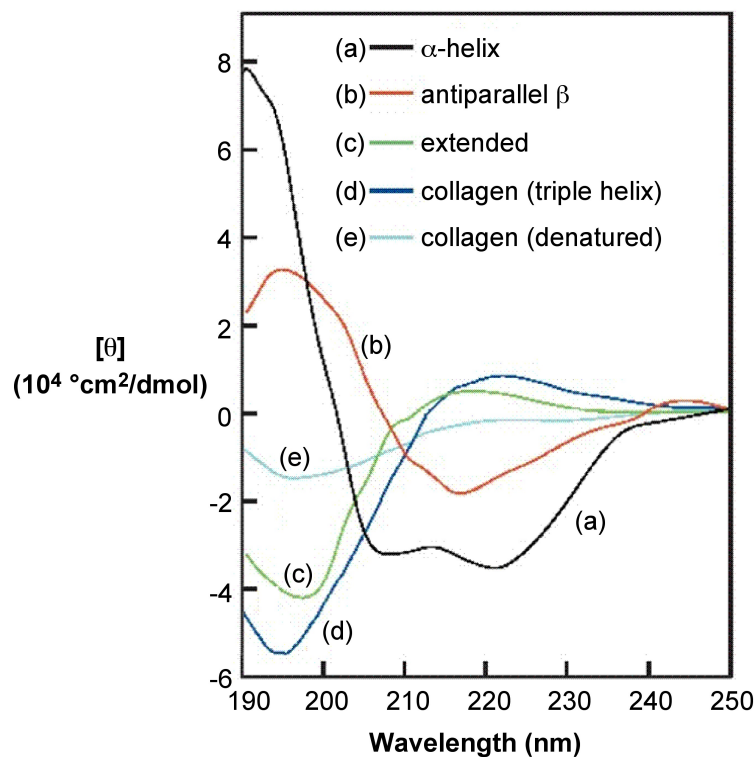


Figure 6.70: CD spectra of samples with representative conformations. Adapted by permission from N. Greenfield, *Nat. Proto.*, 2006, **1**, 6.

Key points for visual estimation of secondary structure by looking at a CD spectrum:

- α -helical proteins have negative bands at 222 nm and 208 nm and a positive band at 193 nm.
- β -helices have negative bands at 218 nm and positive bands at 195 nm.

- Proteins lacking any ordered secondary structure will not have any peaks above 210 nm.

Since the CD spectra of proteins uniquely represent their conformation, CD can be used to monitor structural changes (due to complex formation, folding/unfolding, denaturation because of rise in temperature, denaturants, change in amino acid sequence/mutation, etc.) in dynamic systems and to study kinetics of protein. In other words CD can be used to perform stability investigations and interaction modeling.

6.6.5 CD instrument

Figure 6.71 shows a typical CD instrument.

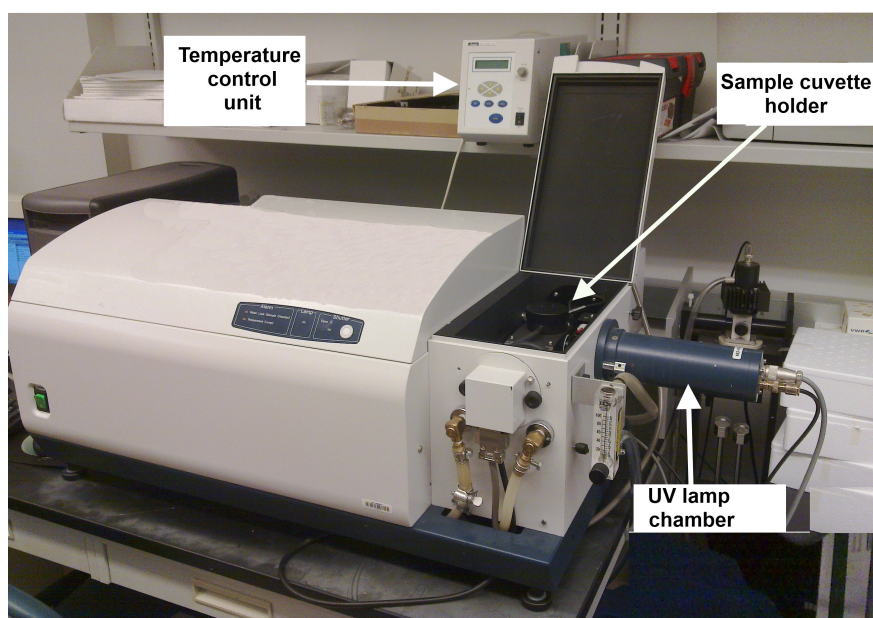


Figure 6.71: A CD instrument.

6.6.6 Protocol for collecting a CD spectrum

Described is a general procedure for data collection, options (time constant of instrument, wavelength interval, half-bandwidth) can be varied according to needs through the instrument controlling program.

6.6.6.1 Sample preparation and starting the instrument

Most of proteins and peptides will require using buffers in order to prevent denaturation. Caution should be shown to avoid using any optically active buffers. Clear solutions are required. CD is taken in high transparency quartz cuvettes to ensure least interference. There are cuvettes available that have path-length ranging from 0.01 cm to 1 cm. Depending on UV activity of buffers used one should choose a cuvette with path-length (distance the beam of light passes through the sample) that compensates for UV absorbance of buffer. Solutions should be prepared according to cuvette that will be used, see Table 6.10.

Cuvette path (cm)	Concentration of sample (mg/mL)
0.01 - 0.02	0.2 – 1.0
0.1	0.05 – 0.2
1	0.005 – 0.01

Table 6.10: Choosing the appropriate cuvette based upon the sample concentration.

Besides, just like salts used to prepare pellets in FT-IR, the buffers in CD will show cutoffs at a certain point in low wavelength region, meaning that buffers start to absorb after certain wavelength. The cutoff values for most of common buffers are known and can be found from manufacturer. Oxygen absorbs light below 200 nm. Therefore, in order to remove interference buffers should be prepared from distilled water or the water should be degassed before use. Another important point is to accurately determine concentration of sample, because concentration should be known for CD data analysis. Concentration of sample can be determined from extinction coefficients, if such are reported in literature also for protein samples quantitative amino acid analysis can be used.

Many CD instrument come bundled with a sample compartment temperature control unit. This is very handy when doing stability and unfolding/denaturation studies of proteins. Check to make sure the heat sink is filled with water. Turn the temperature control unit on and set to chosen temperature.

UV source in CD is very powerful lamp and can generate large amounts of Ozone in its chamber. Ozone significantly reduces the life of the lamp. Therefore, oxygen should be removed before turning on the main lamp (otherwise it will be converted to ozone near lamp). For this purpose nitrogen gas is constantly flushed into lamp compartment. Let Nitrogen flush at least for 15 min. before turning on the lamp.

6.6.6.2 Collecting spectra for blank, water, buffer background, and sample

- Step 1. Collect spectrum of air blank (Figure 6.72). This will be essentially a line lying on x-axis of spectrum, zero absorbance.
- Step 2. Fill the cuvette with water and take a spectrum.
- Step 3. Water droplets left in cuvette may change concentration of your sample, especially when working with dilute samples. Hence, it is important to thoroughly dry the cuvette. After drying the cuvette, collect spectrum of buffer of exactly same concentration as used for sample (Figure 6.72). This is the step where buffer is confirmed to be suitable spectrum of the buffer and water should overlap within experimental error, except for low wavelength region where signal-to-noise ratio is low.
- Step 4. Clean the cuvette as described above and fill with sample solution. Collect the CD spectrum for three times for better accuracy (Figure 6.72). For proteins multiple scans should overlap and not drift with time.

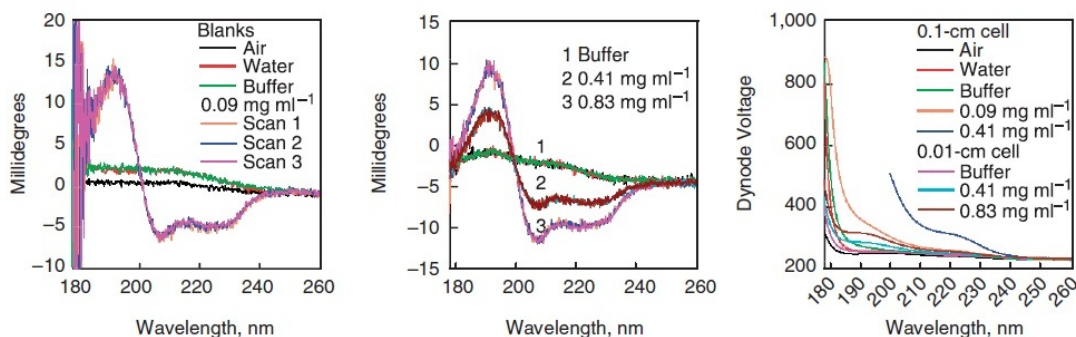


Figure 6.72: CD spectra of blank and water (left), buffer (center), and sample (right). Lysozyme in 10 mM sodium phosphate pH 7. Adapted by permission from N. Greenfield, *Nat. Protoc.*, 2006, **1**, 6.

6.6.6.3 Data handling and analysis

After saving the data for both the spectra of the sample and blank is smoothed using built-in commands of controller software. The smoothed baseline is subtracted from the smoothed spectrum of the sample. The next step is to use software bundles which have algorithms for estimating secondary structure of proteins. Input the data into the software package of choice and process it. The output from algorithms will be the percentage of a particular secondary structure conformation in sample. The data shown in Figure 6.73 lists commonly used methods and compares them for several proteins. The estimated secondary structure is compared to X-ray data, and one can see that it is best to use several methods for best accuracy.

METHOD		X-Ray	LINCOMB		MLR		CONTIN		SELCON		VARSLC		K2D		CDNN
Lowest wavelength, nm			200	178	200	178	200	190	200	178	200	178	200	200	180
Myoglobin	α -helix	78	96	93	89	97	67	89	73	79	76	74	74	83	84
	β -sheet	0	0	0	0	0	0	0	-3	0	0	0	8	3	2
	Turn	10	4	5	8	3	16	0	13	20	4	18	ND	9	9
Lactate dehydrogenase	α -helix	37	46	40	63	42	46	40	41	39	40	39	55	42	44
	β -sheet	14	21	29	15	33	7	39	12	27	15	28	11	13	10
	Turn	25	15	11	13	9	26	1	22	27	17	13		15	14
Chymotrypsin	α -helix	10	15	21	33	28	11	9	7	15	24	16	12	19	20
	β -sheet	38	25	14	6	0	16	32	16	26	0	11	33	29	50
	Turn	26	10	16	5	9	44	32	13	16	42	39	ND	21	22
Bence Jones protein	α -helix	3	0	0	0	0	6	0	3	9	14	0	3	13	16
	β -sheet	50	43	40	68	40	42	81	47	34	7	69	50	39	22
	Turn	24	25	29	17	28	25	10	23	40	28	17	ND	22	22
Lowest wavelength, nm			200	190	200	190	200	190	200	178	200	178	200	200	180
Poly(lys-leu)n	α -helix	0	0	9	0	2	12	9	31	24	31	30	5	34	39
In 0.5 M NaF, pH 7	β -sheet	100	89	65	89	99	73	91	24	39	51	55	89	18	13
	Turn	0	11	26	7	0	0	0	26	26	1	3	ND	16	13
Lowest wavelength, nm			200	190	200	190	200	190	200	190	200	190	200	190	190
Poly-L-lysine 0.01%	α -helix	100	97	100	-	-	100	100	99	89	100	96	100	92	94
helical form, pH 11.1	β -sheet	0	3	0	-	-	0	0	0	1	6	18	0	1	1
In water	Turn	0	0	0	-	-	0	0	1	6	13	15	0	7	7

Figure 6.73: Comparison of secondary structure estimation methods. Adapted by permission from N. Greenfield, *Nat. Protoc.*, 2006, **1**, 6.

6.6.7 Conclusion

What advantages CD has over other analysis methods? CD spectroscopy is an excellent, rapid method for assessing the secondary structure of proteins and performing studies of dynamic systems like folding and binding of proteins. It worth noting that CD does not provide information about the position of those subunits with specific conformation. However, CD outrivals other techniques in rapid assessing of the structure of unknown protein samples and in monitoring structural changes of known proteins caused by ligation and complex formation, temperature change, mutations, denaturants. CD is also widely used to juxtapose fused proteins with wild type counterparts, because CD spectra can tell whether the fused protein retained the structure of wild type or underwent changes.

6.6.8 Bibliography

- L. Que, *Physical Methods in Bioinorganic Chemistry – Spectroscopy and Magnetism*, University Science Books, Sausalito (2000).
- J. P. Wang, J. Nian, L. Xiaoqi, X. Yunhao, and C. S. Hanke, *New J. Phys.*, 2010, **12**, 063032.
- N. Greenfield, *Nat. Protoc.*, 2006, **1**, 6.
- G. Holzwarth and P. Doty, *J. Am. Chem. Soc.*, 1965, **87**, 218.
- N. Greenfield and G.D. Fasman, *Biochemistry*, 1969, **8**, 4108.
- P. Atkins and J. de Paula, *Elements of Physical Chemistry*, 4th ed, Oxford University Press (2005).
- M. Rutherford and M. Dunn, *Curr. Protoc. Protein Sci.*, 2011, **63**, 3.2.1.

6.7 Protein Analysis using Electrospray Ionization Mass Spectroscopy⁸

6.7.1 Introduction

Electrospray ionization-mass spectrometry (ESI-MS) is an analytical method that focuses on macromolecular structural determination. The unique component of ESI-MS is the electrospray ionization. The development of electrospraying, the process of charging a liquid into a fine aerosol, was completed in the 1960's when Malcolm Dole (Figure 6.74) demonstrated the ability of chemical species to be separated through electrospray techniques. With this important turn of events, the combination of ESI and MS was feasible and was later developed by John B. Fenn (Figure 6.75), as a functional analytical method that could provide beneficial information about the structure and size of a protein. Fenn shared the Nobel Prize in 2002, with Koichi Tanaka (Figure 6.76) and Kurt Wüthrich (Figure 6.77) for the development of ESI-MS.

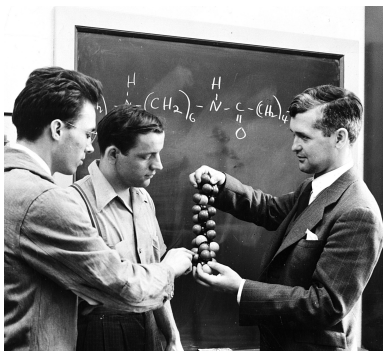


Figure 6.74: American chemist Malcolm Dole (on right) (1903 – 1990).

⁸This content is available online at <<http://cnx.org/content/m38341/1.1/>>.



Figure 6.75: American chemist John Bennett Fenn (1917 - 2010) shared the Nobel Prize for his work in ESI-MS and other identification and structural analyses of biological molecules.



Figure 6.76: Japanese chemist and Nobel laureate Tanaka (1959 -).



Figure 6.77: Swiss chemist and Nobel laureate Kurt W. üthrich (1938 –).

ESI-MS is the process through which proteins, or macromolecules, in the liquid phase are charged and fragmented into smaller aerosol droplets. These aerosol droplets lose their solvent and propel the charged fragments into the gas phase in several components that vary by charge. These components can then be detected by a mass spectrometer. The recent boom and development of ESI-MS is attributed to its benefits in characterizing and analyzing macromolecules, specifically biologically important macromolecules such as proteins.

6.7.2 How does ESI-MS function?

ESI-MS is a process that requires the sample to be in liquid solution, so that tiny droplets may be ionized and analyzed individually by a mass spectrometer. The following delineates the processes that occur as relevant to Figure 6.78:

- **Spray needle/capillary-** The liquid solution of the desired macromolecule is introduced into the system through this needle. The needle is highly charged via an outside voltage source that maintains the charge constant across the needle. The normal charge for a needle is approximately 2.5 to 4 kV. The voltage causes the large droplets to fragment into small droplets based on charge that is accumulated from the protein constituent parts, and the liquid is now in the gas phase.
- **Droplet formation-** The droplets that are expelled from the needle are smaller than initially, and as a result the solvent will evaporate. The smaller droplets then start increasing their charge density on the surface as the volume decreases. As the droplets near the Rayleigh limit, Coulombic interactions of the droplet equal the surface tension of the droplet, a *Coulombic explosion* occurs that further breaks the droplet into minute fractions, including the isolated analyte with charge.
- **Vacuum interface/cone -** This portion of the device allows for the droplets to align in a small trail and pass through to the mass spectrometer. Alignment occurs because of the similarity and differences in charges amongst all the droplets. All the droplets are ionized to positive charges through addition of protons to varying basic sites on the droplets, yet all the charges vary in magnitude dependent upon

the number of basic sites available for protonation. The receiving end or the cone has the opposite charge of the spray needle, causing an attraction between the cone and the droplets.

- Mass spectrometer- The charged particles then reach the mass spectrometer and are deflected based on the charge of each particle. Deflection occurs by the quadrupole magnet of the mass spectrometer. The different deflection paths of the ions occur due to the strength of the interaction with the magnetic field. This leads to various paths based on a mass/charge (m/z) ratio. The particles are then read by the ion detector, as they arrive, providing a spectrum based on m/z ratio.

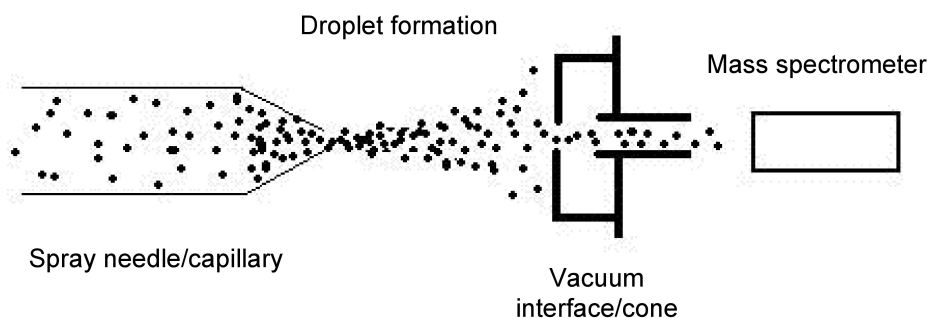


Figure 6.78: The process of ESI-MS. A focus on the capillary spray needle and the generation of aerosol particles.

6.7.3 What data is provided by ESI-MS?

As implied by the name, the data produced from this technique is a mass spectrometry spectrum. Without delving too deeply into the topic of mass spectrometry, which is out of the true scope of this module, a slight explanation will be provided here. The mass spectrometer separates particles based on a magnetic field created by a quadrupole magnet. The strength of the interaction varies on the charge the particles carry. The amount of deflection or strength of interaction is determined by the ion detector and quantified into a mass/charge (m/z) ratio. Because of this information, determination of chemical composition or peptide structure can easily be managed as is explained in greater detail in the following section.

6.7.4 Interpretation of a typical MS spectrum

Interpreting the mass spectrometry data involves understanding the m/z ratio. The knowledge necessary to understanding the interpretation of the spectrum is that the peaks correspond to portions of the whole molecule. That is to say, hypothetically, if you put a human body in the mass spectrometer, one peak would coincide with one arm, another peak would coincide with the arm and the abdomen, etc. The general idea behind these peaks, is that an overlay would paint the entire picture, or in the case of the hypothetical example, provide the image of the human body. The m/z ratio defines these portions based on the charges carried by them; thus the terminology of the mass/charge ratio. The more charges a portion of the macromolecule or protein holds, the smaller the m/z ratio will be and the farther left it will appear on the spectrum. The fundamental concept behind interpretation involves understanding that the peaks are interrelated, and thus the math calculations may be carried out to provide relevant information of the protein or macromolecule being analyzed.

6.7.5 Calculation of m/z of the MS spectrum peaks

As mentioned above, the pertinent information to be obtained from the ESI-MS data is extrapolated from the understanding that the peaks are interrelated. The steps for calculating the data are as follow:

- Step 1. Determine which two neighboring peaks will be analyzed.
- Step 2. Establish the first peak (the one farthest left) as the peak with the greatest m/z ratio. This is mathematically defined as our $z+1$ peak.
- Step 3. Establish the adjacent peak to the right of our first peak as the peak with the lower m/z ratio. This is mathematically our z peak.
- Step 4. Our $z+1$ peak will also be our $m+1$ peak as the difference between the two peaks is the charge of one proton. Consequently, our z peak will be defined as our m peak.
- Step 5. Solve both equations for m to allow for substitution. Both sides of the equation should be in terms of z and can be solved.
- Step 6. Determine the charge of the z peak and subsequently, the charge of the $z+1$ peak.
- Step 7. Subtract one from the m/z ratio and multiply the m/z ratio of each peak by the previous charges determined to obtain the mass of the protein or macromolecule.
- Step 8. Average the results to determine the average mass of the macromolecule or protein.

Example 6.1

- Step 1. Determine which two neighboring peaks will be analyzed from the MS (Figure 6.79) as the $m/z = 5$ and $m/z = 10$ peaks.

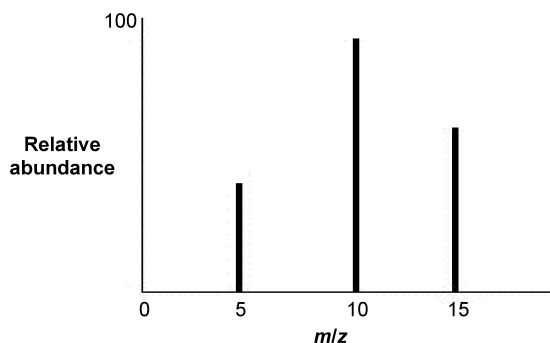


Figure 6.79: Hypothetical mass spectrometry data; not based off of any particular compound. The example steps are based off of this spectrum.

- Step 2. Establish the first peak (the one farthest left in Figure 6.79) as the $z + 1$ peak (i.e., $z + 1 = 5$).
- Step 3. Establish the adjacent peak to the right of the first peak as the z peak (i.e., $z = 10$).
- Step 4. Establish the peak ratios, (6.21) and (6.22).

$$\frac{m+1}{z+1} = 5 \quad (6.21)$$

$$\frac{m}{z} = 10 \quad (6.22)$$

Step 5. Solve the ratios for m : (6.23) and (6.24).

$$m = 5z + 4 \quad (6.23)$$

$$m = 10z \quad (6.24)$$

Step 6. Substitute one equation for m : (6.25).

$$5z + 4 = 10z \quad (6.25)$$

Step 7. Solve for z : (6.26).

$$z = 4/5 \quad (6.26)$$

Step 8. Find $z + 1$: (6.27).

$$z + 1 = 9/5 \quad (6.27)$$

Step 9. Find average molecular mass by subtracting the mass by 1 and multiplying by the charge: (6.28) and (6.29). Hence, the average mass = 7.2.

$$(10 - 1)(4/5) = 7.2 \quad (6.28)$$

$$(5 - 1)(9/5) = 7.2 \quad (6.29)$$

6.7.6 Sample preparation

Samples for ESI-MS must be in a liquid state. This requirement provides the necessary medium to easily charge the macromolecules or proteins into a fine aerosol state that can be easily fragmented to provide the desired outcomes. The benefit to this technique is that solid proteins that were once difficult to analyze, like metallothionein, can dissolved in an appropriate solvent that will allow analysis through ESI-MS. Because the sample is being delivered into the system as a liquid, the capillary can easily charge the solution to begin fragmentation of the protein into smaller fractions. Maximum charge of the capillary is approximately 4 kV. However, this amount of charge is not necessary for every macromolecule. The appropriate charge is dependent on the size and characteristic of the solvent and each individual macromolecule. This has allowed for the removal of the molecular weight limit that was once held true for simple mass spectrometry analysis of proteins. Large proteins and macromolecules can now easily be detected and analyzed through ESI-MS due to the facility with which the molecules can fragment.

6.7.7 Related techniques

A related technique that was developed at approximately the same time as ESI-MS is matrix assisted laser desorption/ionization mass spectrometry (MALDI-MS). This technique that was developed in the late 1980's as well, serves the same fundamental purpose; allowing analysis of large macromolecules via mass spectrometry through an alternative route of generating the necessary gas phase for analysis. In MALDI-MS, a matrix, usually comprised of crystallized 3,5-dimethoxy-4-hydroxycinnamic acid (Figure 6.80), water, and an organic solvent, is used to mix the analyte, and a laser is used to charge the matrix. The matrix then co-crystallizes the analyte and pulses of the laser are then used to cause desorption of the matrix and some of the analyte crystals with it, leading to ionization of the crystals and the phase change into the gaseous state. The analytes are then read by the tandem mass spectrometer. Table 6.11 directly compares some attributes between ESI-MS and MALDI-MS. It should be noted that there are several variations of both ESI-MS and MALDI-MS, with the methods of data collection varying and the piggy-backing of several other methods (liquid chromatography, capillary electrophoresis, inductively coupled plasma mass spectrometry, etc.), yet all of them have the same fundamental principles as these basic two methods.

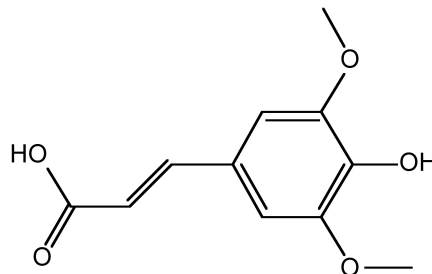


Figure 6.80: Structure of 3,5-dimethoxy-4-hydroxycinnamic acid.

Experimental details	ESI-MS	MALDI-MS
Starting analyte state	Liquid	Liquid/solid
Method of ionization	Charged capillary needle	Matrix laser desorption
Final analyte state	Gas	Gas
Quantity of protein needed	1 μ L	1 μ L
Spectrum method	Mass spectrometry	Mass spectrometry

Table 6.11: Comparison of the general experimental details of ESI-MS and MALDI-MS.

6.7.8 Problems with ESI-MS

ESI-MS has proven to be useful in determination of tertiary structure and molecular weight calculations of large macromolecules. However, there are still several problems incorporated with the technique and macromolecule analysis. One problem is the isolation of the desired protein for analysis. If the protein is unable to be extracted from the cell, this is usually done through gel electrophoresis, there is a limiting factor in what proteins can be analyzed. Cytochrome *c* (Figure 6.81) is an example of a protein that can be isolated

and analyzed, but provides an interesting limitation on how the analytical technique does not function for a completely effective protein analysis. The problem with cytochrome *c* is that even if the protein is in its native confirmation, it can still show different charge distribution. This occurs due to the availability of basic sites for protonation that are consistently exposed to the solvent. Any slight change to the native conformation may cause basic sites, such as in cytochrome *c* to be blocked causing different m/z ratios to be seen. Another interesting limitation is seen when inorganic elements, such as in metallothioneins proteins that contain zinc, are analyzed using ESI-MS. Metallothioneins have several isoforms that show no consistent trend in ESI-MS data between the varied isoforms. The marked differences occur due to the metallation of each isoform being different, which causes the electrospraying and as a result protonation of the protein to be different. Thus, incorporation of metal atoms in proteins can have various effects on ESI-MS data due to the unexpected interactions between the metal center and the protein itself.

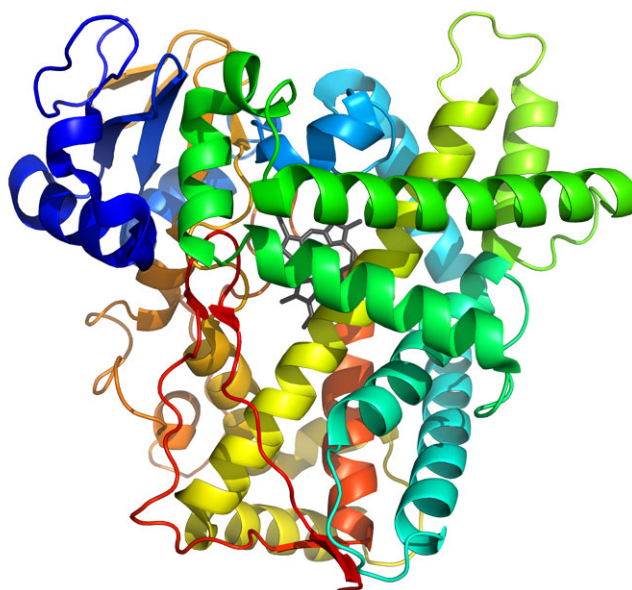


Figure 6.81: The 3-D structure of human cytochrome P450 2A13, a sub class of human cytochrome *c*.

6.7.9 Bibliography

- L. Konermann and D. J. Douglas, *Biochemistry*, 1997, **36**, 12296.
- S. Pérez-Rafael, S. Atrian, M. Capdevila, and Ò. Palacios, *Talanta*, 2011, **83**, 1057.
- D. L. Nelson and M. M. Cox, *Lehninger Principles of Biochemistry*, 5th Ed, W. H. Freeman and Company, New York (2008).
- A. Prange and D. Profrock, *Anal. Bioanal. Chem.*, 2005, **383**, 372.
- <http://www.chm.bris.ac.uk/ms/theory/esi-ionisation.html>⁹

⁹<http://www.chm.bris.ac.uk/ms/theory/esi-ionisation.html>

6.8 The Analysis of Liquid Crystal Phases using Polarized Optical Microscopy¹⁰

6.8.1 Introduction

6.8.1.1 Liquid crystal phases

Liquid crystals are a state of matter that has the properties between solid crystal and common liquid. There are basically three different types of liquid crystal phases:

- Thermotropic liquid crystal phases are dependent on temperature.
- Lyotropic liquid crystal phases are dependent on temperature and the concentration of LCs in the solvent.
- Metallotropic LCs are composed of organic and inorganic molecules, and the phase transition not only depend on temperature and concentration, but also depend on the ratio between organic and inorganic molecules.

Thermotropic LCs are the most widely used one, which can be divided into five categories:

- Nematic phase in which rod-shaped molecules have no positional order, but they self-align to have long-range directional order with their long axes roughly parallel (Figure 6.82a).
- Smectic phase where the molecules are positionally ordered along one direction in well-defined layers oriented either along the layer normal (smectic A) or tilted away from the layer normal (smectic C), see Figure 6.82b).
- Chiral phase which exhibits a twisting of the molecules perpendicular to the director, with the molecular axis parallel to the director (Figure 6.82c).
- Blue phase having a regular three-dimensional cubic structure of defects with lattice periods of several hundred nanometers, and thus they exhibit selective Bragg reflections in the wavelength range of light (Figure 6.83).
- Discotic phase in which disk-shaped LC molecules can orient themselves in a layer-like fashion (Figure 6.84).

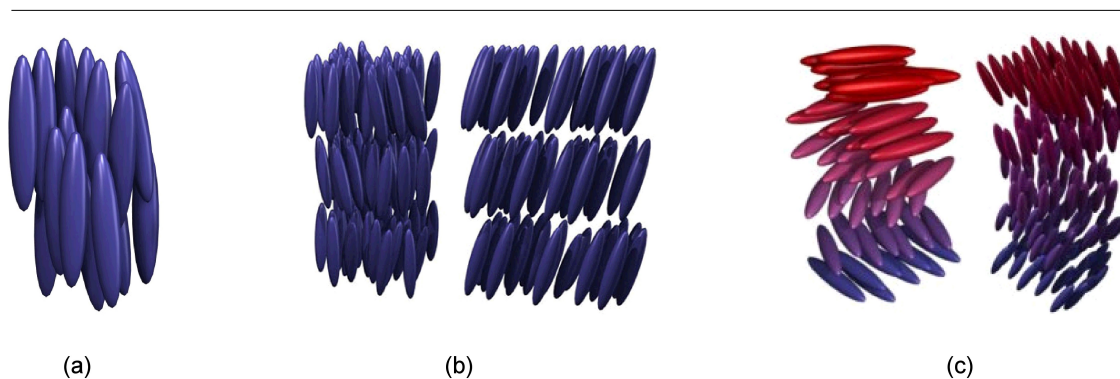


Figure 6.82: Schematic representations of (a) a nematic LC phase, (b) smectic LC phases oriented along (left) and away (right) from the normal of the layer, and (c) a chiral LC phase.

¹⁰This content is available online at <http://cnx.org/content/m38343/1.2/>.

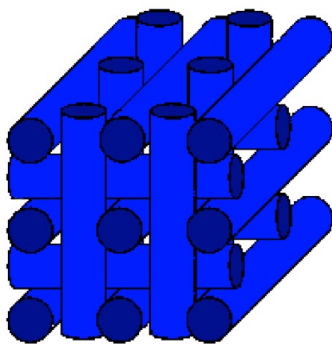


Figure 6.83: A schematic representation of the ordered structure of a blue LC phase.



Figure 6.84: Schematic representations of (a) a discotic nematic LC phase and (b) a discotic columnar LC phase.

Thermotropic LCs are very sensitive to temperature. If the temperature is too high, thermal motion will destroy the ordering of LCs, and push it into a liquid phase. If the temperature is too low, thermal motion is hard to perform, so the material will become crystal phase.

The existence of liquid crystal phase can be detected by using polarized optical microscopy, since liquid crystal phase exhibits its unique texture under microscopy. The contrasting areas in the texture correspond to domains where LCs are oriented towards different directions.

6.8.1.2 Polarized optical microscopy

Polarized optical microscopy is typically used to detect the existence of liquid crystal phases in a solution. The principle of this is corresponding to the polarization of light. A polarizer is a filter that only permits the light oriented in a specific direction with its polarizing direction to pass through. There are two polarizers in a polarizing optical microscope (POM) (Figure 6.85) and they are designed to be oriented at right angle to each other, which is termed as cross polar. The fundamental of cross polar is illustrated in Figure 6.86, the polarizing direction of the first polarizer is oriented vertically to the incident beam, so only the waves with vertical direction can pass through it. The passed wave is subsequently blocked by the second polarizer, since this polarizer is oriented horizontally to the incident wave.

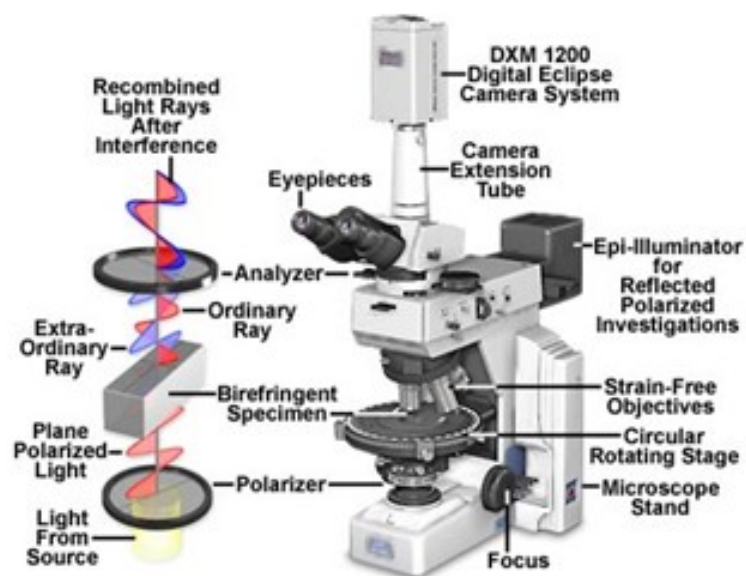


Figure 6.85: The basic configuration of polarized optical microscope. Copyright: Nikon Corporation.

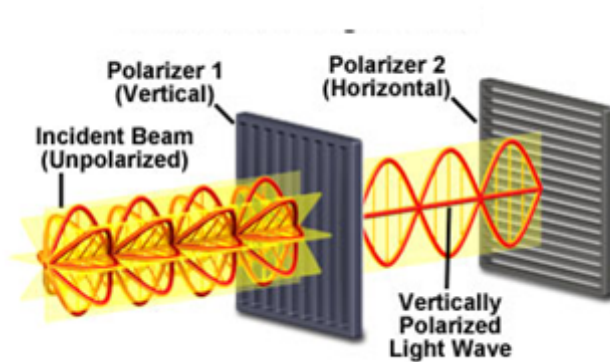


Figure 6.86: A schematic representation of the polarization of light waves. Copyright: Nikon Corporation.

6.8.1.3 Theory of birefringence

Birefringent or doubly-refracting sample has a unique property that it can produce two individual wave components while one wave passes through it, those two components are termed as ordinary and extraordinary waves. Figure 6.88 is an illustration of a typical construction of Nicol polarizing prism, as we can see, the non-polarized white light are splitted into two ray as it passes through the prism. The one travels out of the prism is called ordinary ray, and the other one is called extraordinary ray. So if we have a birefringent specimen located between the polarizer and analyzer, the initial light will be separated into two waves when it passes through the specimen. After exiting the specimen, the light components become out of phase, but are recombined with constructive and destructive interference when they pass through the analyzer. Now the combined wave will have elliptically or circularly polarized light wave, see Figure 6.88, image contrast arises from the interaction of plane-polarized light with a birefringent specimen so some amount of wave will pass through the analyzer and give a bright domain on the specimen.

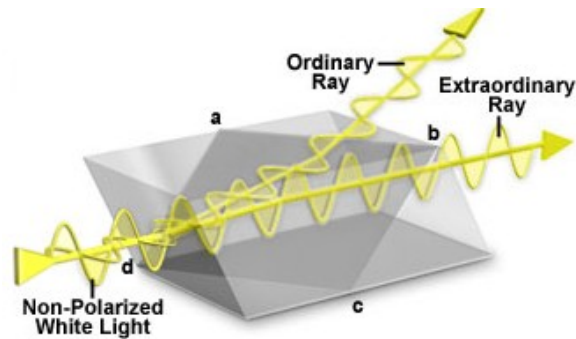


Figure 6.87: A schematic representation of a Nicol polarizing prism. Copyright: Nikon Corporation.

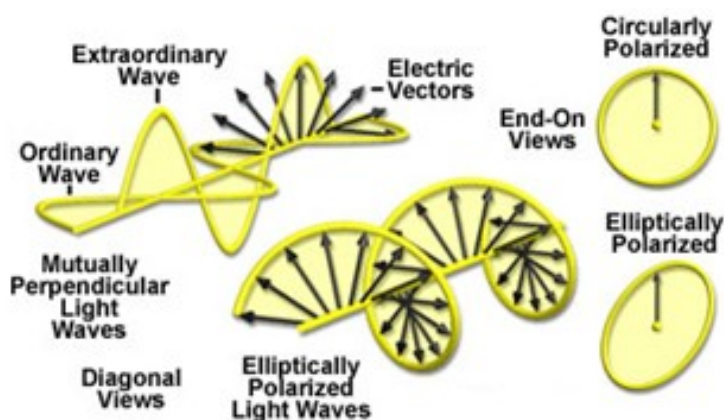


Figure 6.88: A schematic representation of elliptically and circularly polarized light waves. Copyright: Nikon Corporation.

6.8.1.4 Liquid crystal display

The most common application of LCs are in liquid crystals displays (LCD). Figure 6.89 is a simple demonstration of how LCD works in digit calculators. There are two crossed polarizers in this system, and liquid crystal (cholesteric spiral pattern) sandwich with positive and negative charging is located between these two polarizers. When the liquid crystal is charged, waves can pass through without changing orientations. When the liquid crystal is out of charge, waves will be rotated 90° as it passes through LCs so it can pass through the second polarizer. There are seven separately charged electrodes in the LCD, so the LCD can exhibit different numbers from 0 to 9 by adjusting the electrodes. For example, when the upper right and lower left electrodes are charged, we can get 2 on the display.

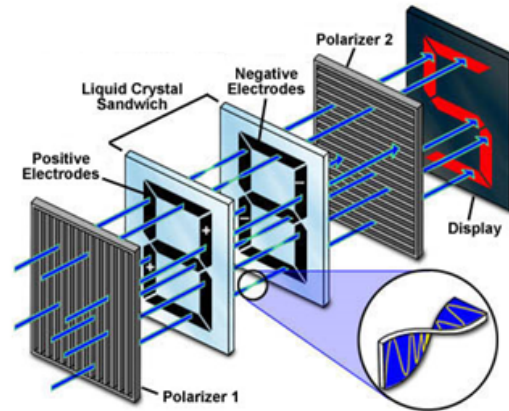


Figure 6.89: Demonstration of a seven-segment liquid crystal display. Copyright: Nikon Corporation.

6.8.2 Microscope images of liquid crystal phase

6.8.2.1 The first order retardation plate

The first order retardation plate is frequently utilized to determine the optical sign of a birefringent specimen in polarized light microscopy. The optical sign includes positive and negative. If the ordinary wavefront is faster than the extraordinary wavefront (see Figure 6.88), the specimen displays positive birefringence. Conversely, a negative birefringence will be detected if the ordinary wavefront is slower than the extraordinary wavefront. In addition, the retardation plate is also useful for enhancing contrast in weakly birefringent specimens. Figure 6.90 shows the effect of first order retardation plate on the contrast of birefringence. The birefringence is so weak that the morphology on the edge of the tissue is hard to image, Figure 6.90a. When a first order retardation plate is added, the structure of the cell become all apparent compared with the one without retardation plate, Figure 6.90b.

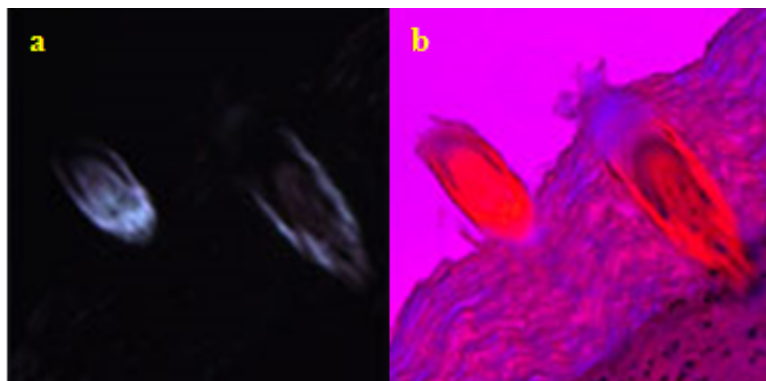


Figure 6.90: Microscope images of thin section of human tongue, (a) without first order retardation plate and (b) with first order retardation plate. Copyright: Olympus.

6.8.2.2 Images of liquid crystal phases

Figure 6.91 shows the images of liquid crystal phases from different specimens. First order retardation plates are utilized in all of these images. Apparent contrasts are detected here in the image which corresponds to the existence of liquid crystal phase within the specimen.

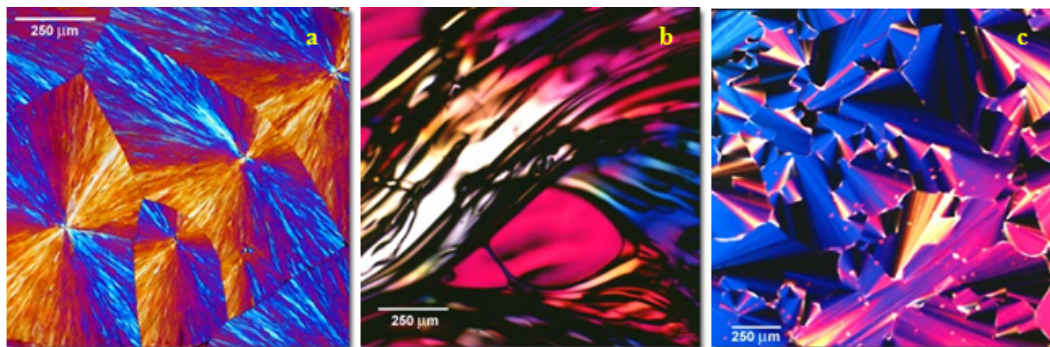


Figure 6.91: Microscope images in polarized light with a first-order retardation plate inserted between the specimen and analyzer: (a) polyethylene glycol, (b) polycarbonate, and (c) liquid crystalline DNA. Copyright from Nikon.

6.8.2.3 The effect of rotation of the polarizer

The effect of the angle between horizontal direction and polarizer transmission axis on the appearance of liquid crystal phase may be analyzed. In Figure 6.92 is shown images of an ascorbic acid (Figure 6.93)

sample under cross polar mode. When the polarizer rotates from 0° to 90° , big variations on the shape of bright domains and domain colors appear due to the change of wave vibrating directions. By rotating the polarizer, we can have a comprehensive understanding of the overall texture.

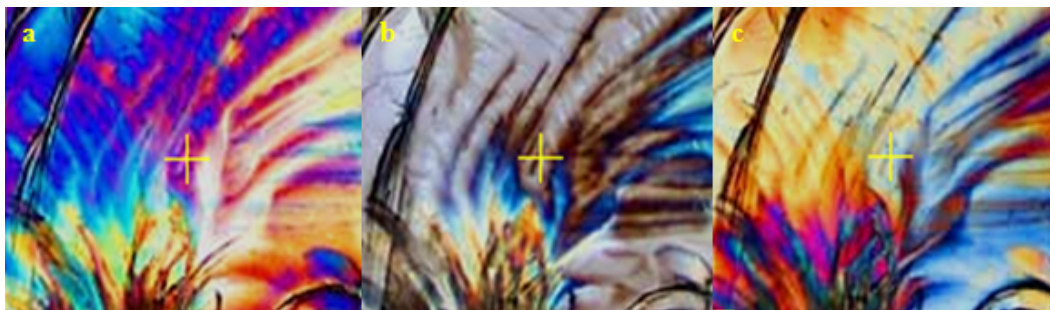


Figure 6.92: Cross polarized Microscope images of ascorbic acid specimen with polarizer rotation of (a) 0° , (b) 45° , and (c) 90° . Copyright: Nikon Corporation.

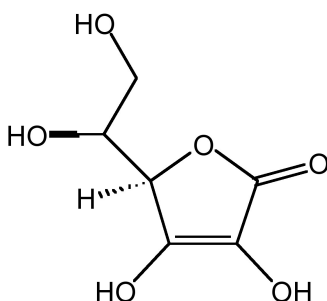


Figure 6.93: The structure of ascorbic acid.

6.8.3 Bibliography

- R. Weaver, *Am. Lab.*, 2003, **35**, 55.
- F. Massoumian, R. Juskaitis, M. A. Neil, and T. Wilson, *J. Microsc.*, 2003, **209**, 13.
- R. Oldenbourg, *Nature*, 1996, **381**, 811.

Chapter 7

Structure at the Nano Scale

7.1 Microparticle Characterization via Confocal Microscopy ¹

7.1.1 A brief history of confocal microscopy

Confocal microscopy was invented by Marvin Minsky (FIGURE) in 1957, and subsequently patented in 1961. Minsky was trying to study neural networks to understand how brains learn, and needed a way to image these connections in their natural state (in three dimensions). He invented the confocal microscope in 1955, but its utility was not fully realized until technology could catch up. In 1973 Egger published the first recognizable cells, and the first commercial microscopes were produced in 1987.



Figure 7.1: American cognitive scientist in the field of artificial intelligence Marvin Lee Minsky (1927 -).

In the 1990's confocal microscopy became near routine due to advances in laser technology, fiber optics, photodetectors, thin film dielectric coatings, computer processors, data storage, displays, and fluorophores. Today, confocal microscopy is widely used in life sciences to study cells and tissues.

¹This content is available online at <<http://cnx.org/content/m34540/1.1/>>.

7.1.2 The basics of fluorescence

Fluorescence is the emission of a secondary photon upon absorption of a photon of higher wavelength. Most molecules at normal temperatures are at the lowest energy state, the so-called 'ground state'. Occasionally, a molecule may absorb a photon and increase its energy to the *excited state*. From here it can very quickly transfer some of that energy to other molecules through collisions; however, if it cannot transfer enough energy it spontaneously emits a photon with a lower wavelength Figure 7.2. This is fluorescence.

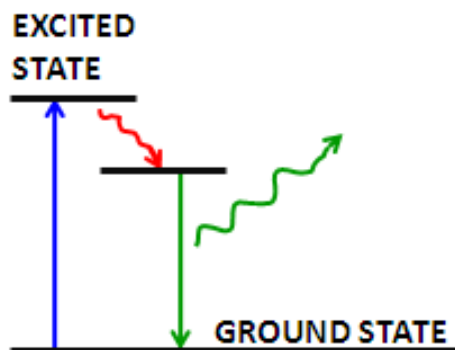


Figure 7.2: An energy diagram shows the principle of fluorescence. A molecule absorbs a high energy photon (blue) which excites the molecule to a higher energy state. The molecule then dissipates some of the extra energy via molecular collisions (red), and emits the remaining energy by emitting a photon (green) to return to the ground state.

In fluorescence microscopy, fluorescent molecules are designed to attach to specific parts of a sample, thus identifying them when imaged. Multiple fluorophores can be used to simultaneously identify different parts of a sample. There are two options when using multiple fluorophores:

- Fluorophores can be chosen that respond to different wavelengths of a multi-line laser.
- Fluorophores can be chosen that respond to the same excitation wavelength but emit at different wavelengths.

In order to increase the signal, more fluorophores can be attached to a sample. However, there is a limit, as high fluorophore concentrations result in them quenching each other, and too many fluorophores near the surface of the sample may absorb enough light to limit the light available to the rest of the sample. While the intensity of incident radiation can be increased, fluorophores may become saturated if the intensity is too high.

Photobleaching is another consideration in fluorescent microscopy. Fluorophores irreversibly fade when exposed to excitation light. This may be due to reaction of the molecules' excited state with oxygen or oxygen radicals. There has been some success in limiting photobleaching by reducing the oxygen available or by using free-radical scavengers. Some fluorophores are more robust than others, so choice of fluorophore is very important. Fluorophores today are available that emit photons with wavelengths ranging 400 - 750 nm.

7.1.3 How confocal microscopy is different from optical microscopy

A microscope's lenses project the sample plane onto an image plane. An image can be formed at many image planes; however, we only consider one of these planes to be the 'focal plane' (when the sample image

is in focus). When a pinhole screen is placed at the image focal point, it allows in-focus light to pass while effectively blocking light from out-of-focus locations Figure 7.3. This pinhole is placed at the conjugate image plane to the focal plane, thus the name "confocal". The size of this pinhole determines the depth-of-focus; a bigger pinhole collects light from a larger volume. The pinhole can only practically be made as small as approximately the radius of the Airy disk, which is the best possible light spot from a circular aperture Figure 7.4, because beyond that more signal is blocked resulting in a decreased signal-to-noise ratio.

NOTE: In optics, the Airy disk and Airy pattern are descriptions of the best focused spot of light that a perfect lens with a circular aperture can make, limited by the diffraction of light.

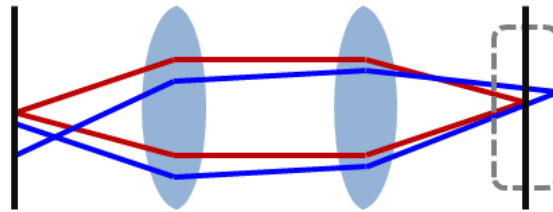


Figure 7.3: A schematic of a simplified microscope objective. Red and blue lines represent light rays refracted through the objective, indicating the focal points and corresponding image points.

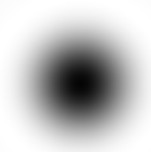


Figure 7.4: A representation of an Airy disk. An intense peak of light forms at the middle, surrounded by rings of lower intensity formed due to the diffraction of light. Adapted with permission from *Confocal Microscopy*, Eric Weeks

To further reduce the effect of scattering due to light from other parts of the sample, the sample is only illuminated at a tiny point through the use of a pinhole in front of the light source. This greatly reduces the interference of scattered light from other parts of the sample. The combination of a pinhole in front of both the light source and detector is what makes confocal unique.

7.1.4 Parts of a confocal microscope

A simple confocal microscope generally consists of a laser, pinhole aperture, dichromatic mirror, scanning mirrors, microscope objectives, a photomultiplier tube, and computing software used to reconstruct the image Figure 7.5. Because a relatively small volume of the sample is being illuminated at any given time, a very bright light source must be used to produce a detectable signal. Early confocal microscopes used zirconium arc lamps, but recent advances in laser technology have made lasers in the UV-visible and infrared more stable and affordable. A laser allows for a monochromatic (narrow wavelength range) light source that can be used to selectively excite fluorophores to emit photons of a different wavelength. Sometimes filters are used to further screen for single wavelengths.

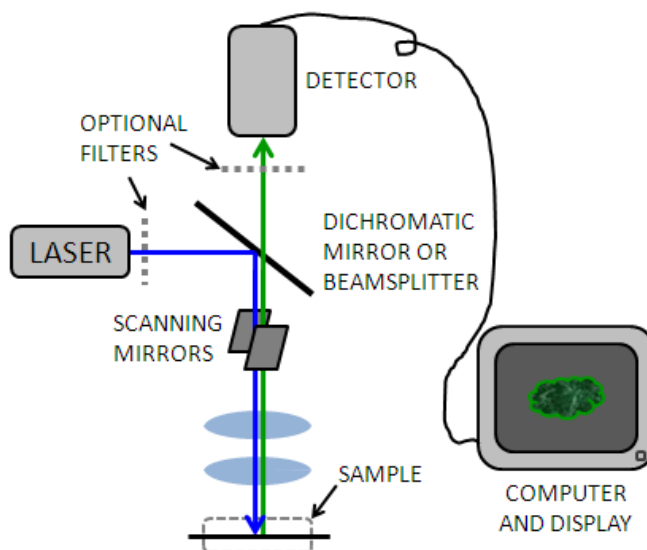


Figure 7.5: A schematic of a confocal microscope. Rays represent the path of light from source to detector.

The light passes through a dichromatic (or "dichroic") mirror Figure 7.5 which allows light with a higher wavelength (from the laser) to pass but reflects light of a lower wavelength (from the sample) to the detector. This allows the light to travel the same path through the majority of the instrument, and eliminates signal due to reflection of the incident light.

The light is then reflects across a pair of mirrors or crystals, one each for the x and y directions, which enable the beam to scan across the sample (Figure 7.5). The speed of the scan is usually the limiting factor in the speed of image acquisition. Most confocal microscopes can create an image in 0.1 - 1 second. Usually the sample is raster scanned quickly in the x -direction and slowly in the y direction (like reading a paragraph left to right, Figure 7.6).

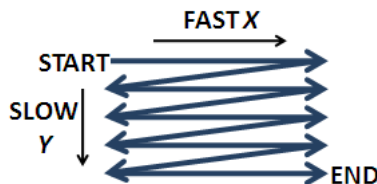


Figure 7.6: Raster scanning is usually performed quickly in the x direction, line-by-line. Other scanning patterns are also used, but this is most common.

The rastering is controlled by galvanometers that move the mirrors back and forth in a sawtooth motion. The disadvantage to scanning with the light beam is that the angle of light hitting the sample changes. Fortunately, this change is small. Interestingly, Minsky's original design moved the stage instead of the beam, as it was difficult to maintain alignment of the sensitive optics. Despite the obvious disadvantages of moving a bulky specimen, there are some advantages of moving the stage and keeping the optics stationary:

- The light illuminates the specimen axially everywhere circumventing optical aberrations, and
- The field of view can be made much larger by controlling the amplitude of the stage movements.

An alternative to light-reflecting mirrors is the acousto-optic deflector (AOD). The AOD allows for fast x -direction scans by creating a diffraction grating from high-frequency standing sound (pressure) waves which locally change the refractive index of a crystal. The disadvantage to AODs is that the amount of deflection depends on the wavelength, so the emission light cannot be descanned (travel back through the same path as the excitation light). The solution to this is to descann only in the y direction controlled by the slow galvanometer and collect the light in a slit instead of a pinhole. This results in reduced optical sectioning and slight distortion due to the loss of radial symmetry, but good images can still be formed. Keep in mind this is not a problem for reflected light microscopy which has the same wavelength for incident and reflected light!

Another alternative is the Nipkow disk, which has a spiral array of pinholes that create the simultaneous sampling of many points in the sample. A single rotation covers the entire specimen several times over (at 40 revolutions per second, that's over 600 frames per second). This allows descanning, but only about 1% of the excitation light passes through. This is okay for reflected light microscopy, but the signal is relatively weak and signal-to-noise ratio is low. The pinholes could be made bigger to increase light transmission but then the optical sectioning is less effective (remember depth of field is dependent on the diameter of the pinhole) and xy resolution is poorer. Highly responsive, efficient fluorophores are needed with this method.

Returning to the confocal microscope (Figure 7.5), light then passes through the objective which acts as a well-corrected condenser and objective combination. The illuminated fluorophores fluoresce and emitted light travels up the objective back to the dichromatic mirror. This is known as epifluorescence when the incident light has the same path as detected light. Since the emitted light now has a lower wavelength than the incident, it cannot pass through the dichromatic mirror and is reflected to the detector. When using reflected light, a beamsplitter is used instead of a dichromatic mirror. Fluorescence microscopy when used properly can be more sensitive than reflected light microscopy.

Though the signal's position is well-defined according to the position of the xy mirrors, the signal from fluorescence is relatively weak after passing through the pinhole, so a photomultiplier tube is used to detect emitted photons. Detecting all photons without regard to spatial position increases the signal, and the photomultiplier tube further increases the detection signal by propagating an electron cascade resulting from the photoelectric effect (incident photons kicking off electrons). The resulting signal is an analog electrical

signal with continuously varying voltage that corresponds to the emission intensity. This is periodically sampled by an analog-to-digital converter.

It is important to understand that the image is a reconstruction of many points sampled across the specimen. At any given time the microscope is only looking at a tiny point, and no complete image exists that can be viewed at an instantaneous point in time. Software is used to recombine these points to form an image plane, and combine image planes to form a 3-D representation of the sample volume.

7.1.5 Two-photon microscopy

Two-photon microscopy is a technique whereby two beams of lower intensity are directed to intersect at the focal point. Two photons can excite a fluorophore if they hit it at the same time, but alone they do not have enough energy to excite any molecules. The probability of two photons hitting a fluorophore at nearly the exact same time (less than 10^{-16}) is very low, but more likely at the focal point. This creates a bright point of light in the sample without the usual cone of light above and below the focal plane, since there are almost no excitations away from the focal point.

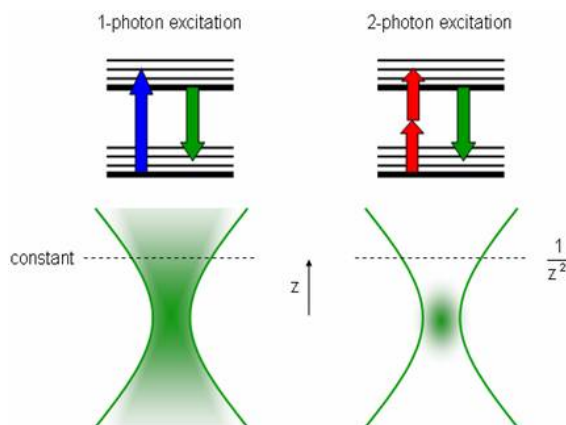


Figure 7.7: Schematic representation of the difference between single photon and two photon microscopy. Copyright: J. Mertz, Boston University.

To increase the chance of absorption, an ultra-fast pulsed laser is used to create quick, intense light pulses. Since the hourglass shape is replaced by a point source, the pinhole near the detector (used to reduce the signal from light originating from outside the focal plane) can be eliminated. This also increases the signal-to-noise ratio (here is very little noise now that the light source is so focused, but the signal is also small). These lasers have lower average incident power than normal lasers, which helps reduce damage to the surrounding specimen. This technique can image deeper into the specimen ($\sim 400 \mu\text{m}$), but these lasers are still very expensive, difficult to set up, require a stronger power supply, intensive cooling, and must be aligned in the same optical table because pulses can be distorted in optical fibers.

7.1.6 Microparticle characterization

Confocal microscopy is very useful for determining the relative positions of particles in three dimensions Figure 7.8. Software allows measurement of distances in the 3D reconstructions so that information about spacing can be ascertained (such as packing density, porosity, long range order or alignment, etc.).

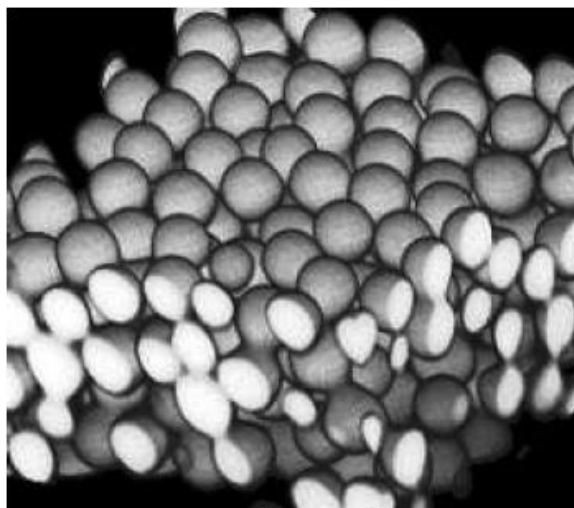


Figure 7.8: A reconstruction of a colloidal suspension of poly(methyl methacrylate) (PMMA) microparticles approximately 2 microns in diameter. Adapted from *Confocal Microscopy of Colloids*, Eric Weeks.

If imaging in fluorescence mode, remember that the signal will only represent the locations of the individual fluorophores. There is no guarantee fluorophores will completely attach to the structures of interest or that there will not be stray fluorophores away from those structures. For microparticles it is often possible to attach the fluorophores to the shell of the particle, creating hollow spheres of fluorophores. It is possible to tell if a sample sphere is hollow or solid but it would depend on the transparency of the material.

Dispersions of microparticles have been used to study nucleation and crystal growth, since colloids are much larger than atoms and can be imaged in real-time. Crystalline regions are determined from the order of spheres arranged in a lattice, and regions can be distinguished from one another by noting lattice defects.

Self-assembly is another application where time-dependent, 3-D studies can help elucidate the assembly process and determine the position of various structures or materials. Because confocal is popular for biological specimens, the position of nanoparticles such as quantum dots in a cell or tissue can be observed. This can be useful for determining toxicity, drug-delivery effectiveness, diffusion limitations, etc.

7.1.7 A summary of confocal microscopy's strengths and weaknesses

Strengths

- Less haze, better contrast than ordinary microscopes.
- 3-D capability.
- Illuminates a small volume.
- Excludes most of the light from the sample not in the focal plane.
- Depth of field may be adjusted with pinhole size.
- Has both reflected light and fluorescence modes.
- Can image living cells and tissues.
- Fluorescence microscopy can identify several different structures simultaneously.
- Accommodates samples with thickness up to 100 μm .
- Can use with two-photon microscopy.

- Allows for optical sectioning (no artifacts from physical sectioning) 0.5 - 1.5 μm .

Weakness

- Images are scanned slowly (one complete image every 0.1-1 second).
- Must raster scan sample, no complete image exists at any given time.
- There is an inherent resolution limit because of diffraction (based on numerical aperture, $\sim 200\text{ nm}$).
- Sample should be relatively transparent for good signal.
- High fluorescence concentrations can quench the fluorescent signal.
- Fluorophores irreversibly photobleach.
- Lasers are expensive.
- Angle of incident light changes slightly, introducing slight distortion.

7.1.8 Bibliography

- P. Davidovits and M. D. Egger, *Nature*, 1973, **244**, 366.
- A. Hibbs, *Confocal Microscopy for Biologists*, Twayne Publishers, Boston (2004).
- M. Minsky, *Scanning*, 1988, **10**, 128.
- J. Pawley, *Handbook of Biological Confocal Microscopy*, Twayne Publishers, Boston (2006).
- V. Prasad, D. Semwogerere, and E.R. Weeks, *J. Phys.: Condens. Matter*, 2007, **19**, 113102.
- D. Semwogerere and E. R. Weeks, *Encyclopedia of Biomaterials and Biomedical Engineering Confocal Microscopy*, Taylor Francis (2005).
- C. Sheppard, *Confocal Laser Scanning Microscopy*, Twayne Publishers, Boston (1997).

7.2 Transmission Electron Microscopy

7.2.1 Transmission Electron Microscopy: An Overview²

Transmission electron microscopy (TEM) is a form of microscopy in which a beam of electrons transmits through an extremely thin specimen, and then interacts with the specimen when passing through it. The formation of images in a TEM can be explained by an optical electron beam diagram in Figure 7.9. TEMs provide images with significantly higher resolution than visible-light microscopes (VLMs) do because of the smaller de Broglie wavelength of electrons. These electrons allow for the examination of finer details, which are several thousand times higher than the highest resolution in a VLM. Nevertheless, the magnification provided in a TEM image is in contrast to the absorption of the electrons in the material, which is primarily due to the thickness or composition of the material.

²This content is available online at <<http://cnx.org/content/m34523/1.1/>>.

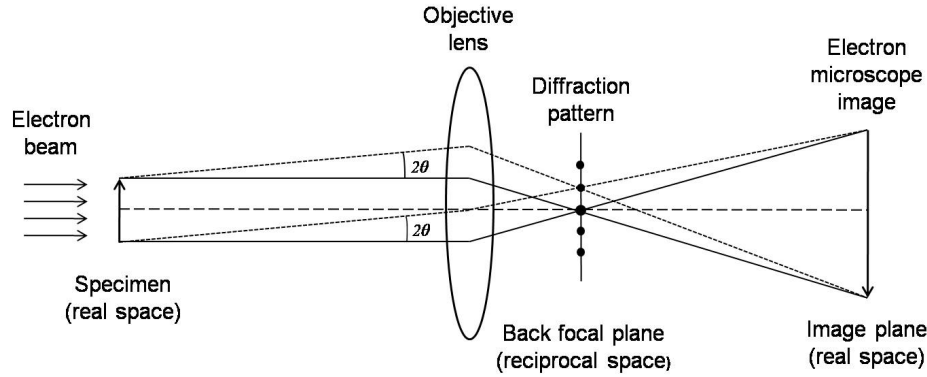


Figure 7.9: The optical electron beam diagram of TEM.

When a crystal lattice spacing (d) is investigated with electrons with wavelength λ , diffracted waves will be formed at specific angles 2θ , satisfying the Bragg condition, (7.1).

$$2d\sin\theta = \lambda \quad (7.1)$$

The regular arrangement of the diffraction spots, the so-called diffraction pattern (DP), can be observed. While the transmitted and the diffracted beams interfere on the image plane, a magnified image (electron microscope image) appears. The plane where the DP forms is called the *reciprocal space*, which the image plane is called the *real space*. A Fourier transform can mathematically transform the real space to reciprocal space.

By adjusting the lenses (changing their focal lengths), both electron microscope images and DP can be observed. Thus, both observation modes can be successfully combined in the analysis of the microstructures of materials. For instance, during investigation of DPs, an electron microscope image is observed. Then, by inserting an aperture (selected area aperture), adjusting the lenses, and focusing on a specific area that we are interested in, we will get a DP of the area. This kind of observation mode is called a *selected area diffraction*. In order to investigate an electron microscope image, we first observe the DP. Then by passing the transmitted beam or one of the diffracted beams through a selected aperture and changing to the imaging mode, we can get the image with enhanced contrast, and precipitates and lattice defects can easily be identified.

Describing the resolution of a TEM in terms of the classic Rayleigh criterion for VLMs, which states that the smallest distance that can be investigated, δ , is given approximately by (7.2), where λ is the wavelength of the electrons, μ is the refractive index of the viewing medium, and β is the semi-angle of collection of the magnifying lens.

$$\delta = \frac{0.61\lambda}{\mu \sin\beta} \quad (7.2)$$

According to de Broglie's ideas of the wave-particle duality, the particle momentum p is related to its wavelength λ through Planck's constant h , (7.3).

$$\lambda = \frac{h}{p} \quad (7.3)$$

Momentum is given to the electron by accelerating it through a potential drop, V , giving it a kinetic energy,

eV. This potential energy is equal to the kinetic energy of the electron, (7.4).

$$eV = \frac{m_o v^2}{2} \quad (7.4)$$

Based upon the foregoing, we can equate the momentum (p) to the electron mass (m_o), multiplied by the velocity (v) and substituting for v from (7.4), i.e., (7.5).

$$p = m_o v = (2m_o eV)^{\frac{1}{2}} \quad (7.5)$$

These equations define the relationship between the electron wavelength, λ , and the accelerating voltage of the electron microscope (V), Eq. However, we have to consider about the relative effects when the energy of electron more than 100 keV. So in order to be exact we must modify (7.6) to give (7.7).

$$\lambda = \frac{h}{(2m_o eV)^{\frac{1}{2}}} \quad (7.6)$$

$$\lambda = \frac{h}{\left[2m_o eV \left(1 + \frac{eV}{2m_o e^2}\right)\right]^{\frac{1}{2}}} \quad (7.7)$$

From (7.2) and (7.7), if a higher resolution is desired a decrease in the electron wavelength is accomplished by increasing the accelerating voltage of the electron microscope. In other words, the higher accelerating rating used, the better resolution obtained.

7.2.1.1 Why the specimen should be thin

The scattering of the electron beam through the material under study can form different angular distribution (Figure 7.10) and it can be either forward scattering or back scattering. If an electron is scattered $< 90^\circ$, then it is forward scattered, otherwise, it is backscattered. If the specimen is thicker, fewer electrons are forward scattered and more are backscattered. Incoherent, backscattered electrons are the only remnants of the incident beam for bulk, non-transparent specimens. The reason that electrons can be scattered through different angles is related to the fact that an electron can be scattered more than once. Generally, the more times of scattering happen, the greater the angle of scattering.

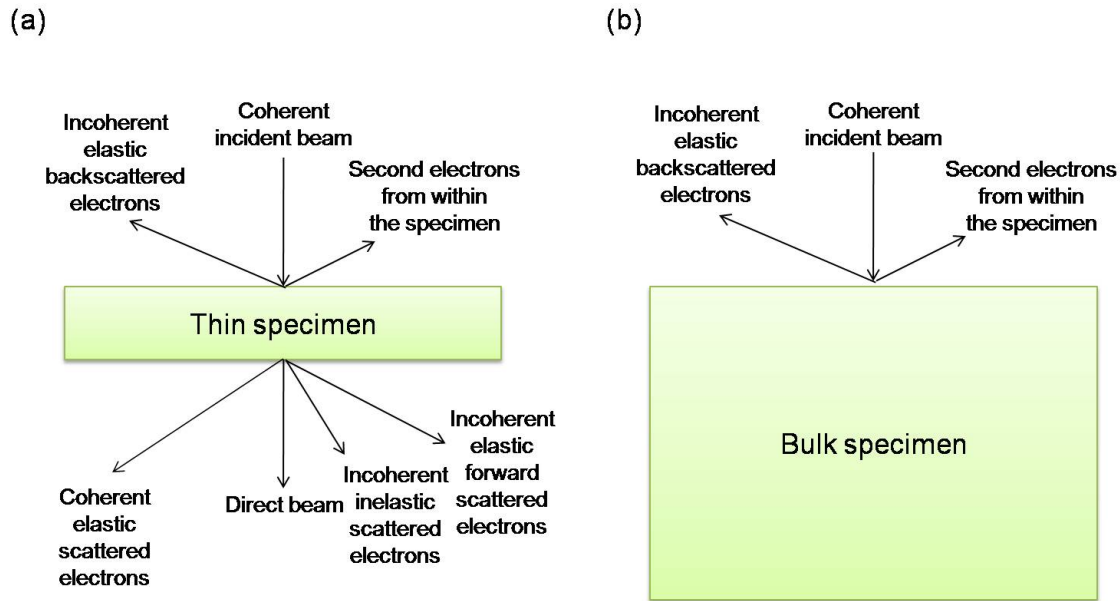


Figure 7.10: Two different kinds of electron scattering from (a) a thin specimen and (b) a bulk specimen.

All scattering in the TEM specimen is often approximated as a single scattering event since it is the simplest process. If the specimen is very thin, this assumption will be reasonable enough. If the electron is scattered more than once, it is called 'plural scattering.' It is generally safe to assume single scattering occurs, unless the specimen is particularly thick. When the times of scattering increase, it is difficult to predict what will happen to the electron and to interpret the images and DPs. So, the principle is 'thinner is better', i.e., if we make thin enough specimens so that the single-scattering assumption is plausible, and the TEM research will be much easier.

In fact, forward scattering includes the direct beam, most elastic scattering, refraction, diffraction, particularly Bragg diffraction, and inelastic scattering. Because of forward scattering through the thin specimen, a DP or an image would be showed on the viewing screen, and an X-ray spectrum or an electron energy-loss spectrum can be detected outside the TEM column. However, backscattering still cannot be ignored, it is an important imaging mode in the SEM.

7.2.1.2 Limitations of TEM

7.2.1.2.1 Interpreting transmission images

One significant problem that might encounter when TEM images are analyzed is that the TEM present us with 2D images of a 3D specimen, viewed in transmission. This problem can be illustrated by showing a picture of two rhinos side by side such that the head of one appears attached to the rear of the other (Figure 7.11).

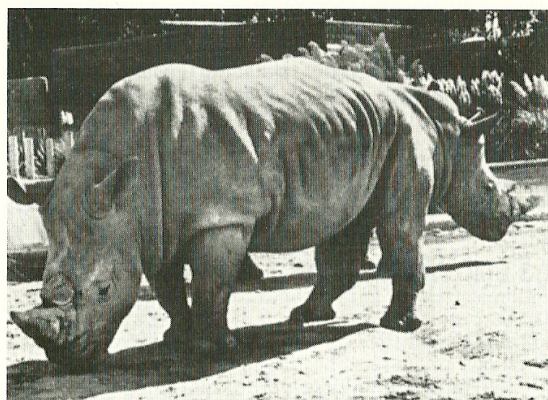


Figure 7.11: In projection, this photograph of two rhinos appears as one two-headed beast, because sometimes people have difficulty to translate a 2D image to a 3D image. Adapted from D. B. Williams and C. B. Carter, *Transmission Electron Microscopy: A Textbook for Material Science*, 2nd Ed., Springer, New York (2009).

One aspect of this particular drawback is that a single TEM image has no depth sensitivity. There often is information about the top and bottom surfaces of the specimen, but this is not immediately apparent. There has been progress in overcoming this limitation, by the development of electron tomography, which uses a sequence of images taken at different angles. In addition, there has been improvement in specimen-holder design to permit full 360° rotation and, in combination with easy data storage and manipulation; nanotechnologists have begun to use this technique to look at complex 3D inorganic structures such as porous materials containing catalyst particles.

7.2.1.2.2 Electron beam damage

A detrimental effect of ionizing radiation is that it can damage the specimen, particularly polymers (and most organics) or certain minerals and ceramics. Some aspects of beam damage made worse at higher voltages. Figure 7.12 shows an area of a specimen damaged by high-energy electrons. However, the combination of more intense electron sources with more sensitive electron detectors, and the use computer enhancement of noisy images, can be used to minimize the total energy received by the sample.

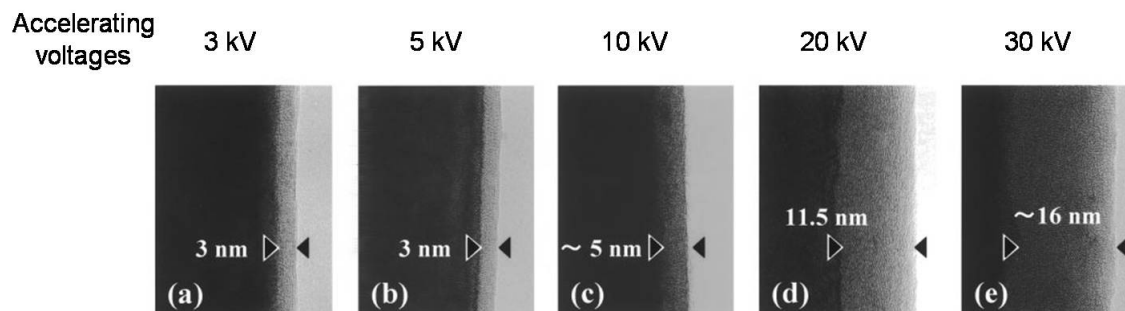


Figure 7.12: High-resolution TEM images at the slit edge of the GaAs samples prepared by slit focused ion beam. GaAs samples prepared at (a) 3 kV, (b) 5 kV, (c) 10 kV, (d) 20 kV, and (e) 30 kV. The thickness of the amorphous layer produced by focused ion beam is shown in each image. Adapted from Y. Yabuuchi, S. Tametou, T. Okano, S. Inazato, S. Sadayamn, and Y. Tamamoto, *J. Electron Microsc.*, 2004, **53**, 5.

7.2.1.3 Sample preparation

The specimens under study have to be thin if any information is to be obtained using transmitted electrons in the TEM. For a sample to be transparent to electrons, the sample must be thin enough to transmit sufficient electrons such that enough intensity falls on the screen to give an image. This is a function of the electron energy and the average atomic number of the elements in the sample. Typically for 100 keV electrons, a specimen of aluminum alloy up to $\sim 1 \mu\text{m}$ would be thin, while steel would be thin up to about several hundred nanometers. However, thinner is better and specimens $< 100 \text{ nm}$ should be used wherever possible.

The method to prepare the specimens for TEM depends on what information is required. In order to observe TEM images with high resolution, it is necessary to prepare thin films without introducing contamination or defects. For this purpose, it is important to select an appropriate specimen preparation method for each material, and to find an optimum condition for each method.

7.2.1.3.1 Crushing

A specimen can be crushed with an agate mortar and pestle. The flakes obtained are suspended in an organic solvent (e.g., acetone), and dispersed with a sonic bath or simply by stirring with a glass stick. Finally, the solvent containing the specimen flakes is dropped onto a grid. This method is limited to materials which tend to cleave (e.g., mica).

7.2.1.3.2 Electropolishing

Slicing a bulk specimen into wafer plates of about 0.3 mm thickness by a fine cutter or a multi-wire saw. The wafer is further thinned mechanically down to about 0.1 mm in thickness. Electropolishing is performed in a specific electrolyte by supplying a direct current with the positive pole at the thin plate and the negative pole at a stainless steel plate. In order to avoid preferential polishing at the edge of the specimen, all the edges are covered with insulating paint. This is called the window method. The electropolishing is finished when there is a small hole in the plate with very thin regions around it (Figure 7.13). This method is mainly used to prepare thin films of metals and alloys.

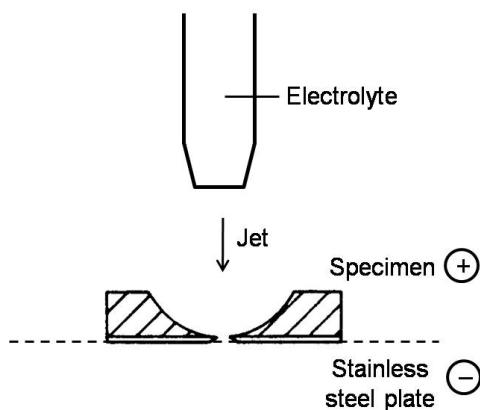


Figure 7.13: Principle of jet electropolishing method. The specimen and the stainless steel plate is electronic positive and negative, respectively.

7.2.1.3.3 Chemical polishing

Thinning is performed chemically, i.e., by dipping the specimen in a specific solution. As for electropolishing, a thin plate of 0.1~0.2 mm in thickness should be prepared in advance. If a small dimple is made in the center of the plate with a dimple grinder, a hole can be made by etching around the center while keeping the edge of the specimen relatively thick. This method is frequently used for thinning semiconductors such as silicon. As with electro-polishing, if the specimen is not washed properly after chemical etching, contamination such as an oxide layer forms on the surface.

7.2.1.3.4 Ultramicrotomy

Specimens of thin films or powders are usually fixed in an acrylic or epoxy resin and trimmed with a glass knife before being sliced with a diamond knife. This process is necessary so that the specimens in the resin can be sliced easily by a diamond knife. Acrylic resins are easily sliced and can be removed with chloroform after slicing. When using an acrylic resin, a gelatin capsule is used as a vessel. Epoxy resin takes less time to solidify than acrylic resins, and they remain strong under electron irradiation. This method has been used for preparing thin sections of biological specimens and sometimes for thin films of inorganic materials which are not too hard to cut.

7.2.1.3.5 Ion milling

A thin plate (less than 0.1 mm) is prepared from a bulk specimen by using a diamond cutter and by mechanical thinning. Then, a disk 3 mm in diameter is made from the plate using a diamond knife or a ultrasonic cutter, and a dimple is formed in the center of the surface with a dimple grinder. If it is possible to thin the disk directly to 0.03 mm in thickness by mechanical thinning without using a dimple grinder, the disk should be strengthened by covering the edge with a metal ring. Ar ions are usually used for the sputtering, and the incidence angle against the disk specimen and the accelerating voltage are set as 10 - 20° and a few kilovolts, respectively. This method is widely used to obtain thin regions of ceramics and semiconductors in particular, and also for cross section of various multilayer films.

7.2.1.3.6 Focused ion beam (FIB)

This method was originally developed for the purpose of fixing semiconductor devices. In principle, ion beams are sharply focused on a small area, and the specimen is thinned very rapidly by sputtering. Usually Ga ions are used, with an accelerating voltage of about 30 kV and a current of about 10 A/cm². The probe size is several tens of nanometers. This method is useful for specimens containing a boundary between different materials, where it may be difficult to homogeneously thin the boundary region by other methods such as ion milling.

7.2.1.3.7 Vacuum evaporation

The specimen to be studied is set in a tungsten-coil or basket. Resistance heating is applied by an electric current passing through the coil or basket, and the specimen is melted, then evaporated (or sublimed), and finally deposited onto a substrate. The deposition process is usually carried under a pressure of 10⁻³-10⁻⁴ Pa, but in order to avoid surface contamination, a very high vacuum is necessary. A collodion film or cleaved rock salt is used as a substrate. Rock salt is especially useful in forming single crystals with a special orientation relationship between each crystal and the substrate. Salt is easily dissolved in water, and then the deposited films can be fixed on a grid. Recently, as an alternative to resistance heating, electron beam heating or an ion beam sputtering method has been used to prepare thin films of various alloys. This method is used for preparing homogeneous thin films of metals and alloys, and is also used for coating a specimen with the metal of alloy.

7.2.1.3.8 The characteristics of the grid

The types of TEM specimens that are prepared depend on what information is needed. For example, a self-supporting specimen is one where the whole specimen consists of one material (which may be a composite). Other specimens are supported on a grid or on a Cu washer with a single slot. Some grids are shown in Figure 7.14. Usually the specimen or grid will be 3 mm in diameter.

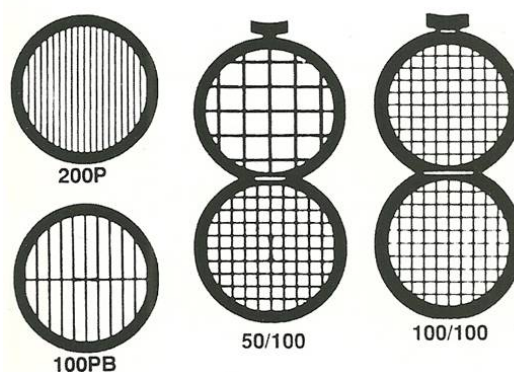


Figure 7.14: TEM sample support mesh grids. A diameter of a grid is usually 3.05 mm, however, some grids with diameters of 2.30 mm are also used for earlier microscopes. Adapted from D. B. Williams and C. B. Carter, *Transmission Electron Microscopy: A Textbook for Material Science*, 2nd Ed., Springer, New York (2009).

TEM specimen stage designs include airlocks to allow for insertion of the specimen holder into the vacuum with minimal increase in pressure in other areas of the microscope. The specimen holders are adapted to

hold a standard size of grid upon which the sample is placed or a standard size of self-supporting specimen. Standard TEM grid sizes is a 3.05 mm diameter ring, with a thickness and mesh size ranging from a few to 100 μm . The sample is placed onto the inner meshed area having diameter of approximately 2.5 mm. The grid materials usually are copper, molybdenum, gold or platinum. This grid is placed into the sample holder which is paired with the specimen stage. A wide variety of designs of stages and holders exist, depending upon the type of experiment being performed. In addition to 3.05 mm grids, 2.3 mm grids are sometimes, if rarely, used. These grids were particularly used in the mineral sciences where a large degree of tilt can be required and where specimen material may be extremely rare. Electron transparent specimens have a thickness around 100 nm, but this value depends on the accelerating voltage.

Once inserted into a TEM, the sample is manipulated to allow study of the region of interest. To accommodate this, the TEM stage includes mechanisms for the translation of the sample in the XY plane of the sample, for Z height adjustment of the sample holder, and usually at least one rotation degree of freedom. Most TEMs provide the ability for two orthogonal rotation angles of movement with specialized holder designs called double-tilt sample holders.

A TEM stage is required to have the ability to hold a specimen and be manipulated to bring the region of interest into the path of the electron beam. As the TEM can operate over a wide range of magnifications, the stage must simultaneously be highly resistant to mechanical drift as low as a few nm/minute while being able to move several μm /minute, with repositioning accuracy on the order of nanometers.

7.2.1.4 Bibliography

- D. B. Williams and C. B. Carter, *Transmission Electron Microscopy: A Textbook for Material Science*, 2nd Ed., Springer, New York (2009).
- D. Shindo and K. Hiraga, *High-Resolution Electron Microscopy for Material Science*, Springer, New York (1998).
- L. Reimer and H. Kohl, *Transmission Electron Microscopy Physics of Image Formation*, 5th Ed., Springer, New York (2008).
- D. L. Spector and R. D. Goldman, *Basic Methods in Microscopy Protocols and Concepts from Cells: A Laboratory Manual*, Cold Spring Harbor, New York (2006).
- Y. Yabuuchi, S. Tametou, T. Okano, S. Inazato, S. Sadayamn, and Y. Tamamoto, *J. Electron Microsc.*, 2004, **53**, 5.

7.2.2 Transmission Electron Microscopy Image for Multilayer-Nanomaterials³

Although, TEMs can only provide 2D analysis for a 3D specimen; magnifications of 300,000 times can be routinely obtained for many materials making it an ideal method for the study of nanomaterials. Besides from the TEM images, darker areas of the image show that the sample is thicker or denser in these areas, so we can observe the different components and structures of the specimen by the difference of color. For investigating multilayer-nanomaterials, a TEM is usually the first choice, because not only does it provide a high resolution image for nanomaterials but also it can distinguish each layer within a nanostructured material.

7.2.2.1 Observations of multilayer-nanomaterials

TEM was been used to analyze the depth-graded W/Si multilayer films. Multilayer films were grown on polished, 100 mm thick Si wafers by magnetron sputtering in argon gas. The individual tungsten and silicon layer thicknesses in periodic and depth-graded multilayers are adjusted by varying the computer-controlled rotational velocity of the substrate platen. The deposition times required to produce specific layer thicknesses were determined from detailed rate calibrations. Samples for TEM were prepared by focused ion

³This content is available online at <<http://cnx.org/content/m34524/1.1/>>.

beam milling at liquid N₂ temperature to prevent any beam heating which might result in re-crystallization and/or re-growth of any amorphous or fine grained polycrystalline layers in the film.

TEM measurements were made using a JEOL-4000 high-resolution transmission electron microscope operating at 400 keV; this instrument has a point-to-point resolution of 0.16 nm. Large area cross-sectional images of a depth-graded multilayer film obtained under medium magnification (~ 100 kX) were acquired at high resolution. A cross-sectional TEM image showed 150 layers W/Si film with the thickness of layers in the range of 3.33 $\sim$ 29.6 nm (Figure 7.15 shows a part of layers). The dark layers are tungsten and the light layers are silicon and they are separated by the thin amorphous W–Si interlayers (gray bands). By the high resolution of the TEM and the nature characteristics of the material, each layer can be distinguished clearly with their different darkness.

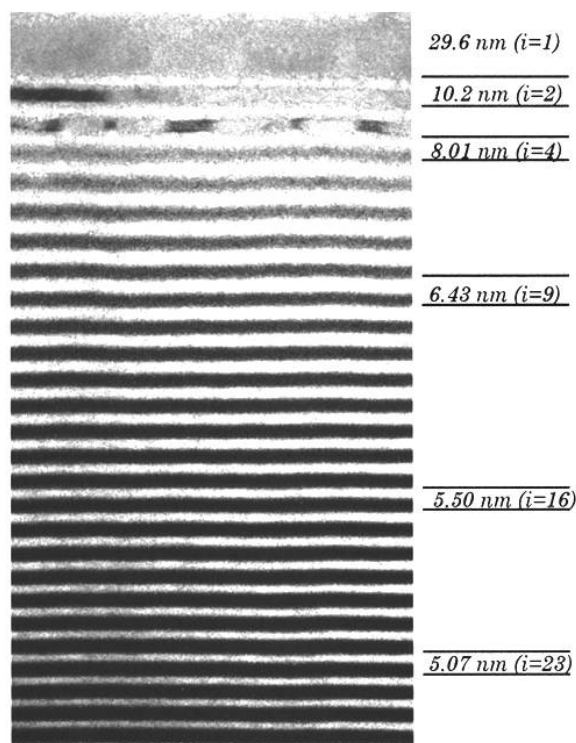


Figure 7.15: Cross-sectional transmission electron micrograph of the top portion of a depth-graded W/Si multilayer structure. Selected bilayer indices and thicknesses are indicated. The tungsten (dark bands) and silicon (light bands) layers are separated by thin amorphous W–Si interlayers (gray bands). The topmost silicon layer is not completely visible in this image. Adapted from D. L. Windt, F. E. Christensen, W. W. Craig, C. Hailey, F. A. Harrison, M. Jimenez-Garate, R. Kalyanaraman, and P. H. Mao, *J. Appl. Phys.*, 2000, **88**, 460.

Not all kinds of multilayer nanomaterials can be observed clearly under TEM. A materials consist of pc-Si:H multilayers were prepared by a photo-assisted chemical vapor deposition (photo-CVD) using a low-pressure mercury lamp as an UV light source to dissociate the gases. The pc-Si:H multilayer included low H₂-diluted a-Si:H sublayers (SL's) and highly H₂-diluted a-Si:H sublayers (SH's). Control of the CVD gas flow (H₂|SiH₄) under continuous UV irradiation resulted in the deposition of multilayer films layer by layer.

For a TEM measurement, a 20 nm thick undiluted a-Si:H film on a c-Si wafer before the deposition

of multilayer to prevent from any epitaxial growth. Figure 7.16 shows a cross-sectional TEM image of a six-cycled pc-Si:H multilayer specimen. The white dotted lines are used to emphasize the horizontal stripes, which have periodicity in the TEM image. As can be seen, there are no significant boundaries between SL and SH could be observed because all sublayers are prepared in H_2 gas. In order to get the more accurate thickness of each sublayer, other measurements might be necessary.

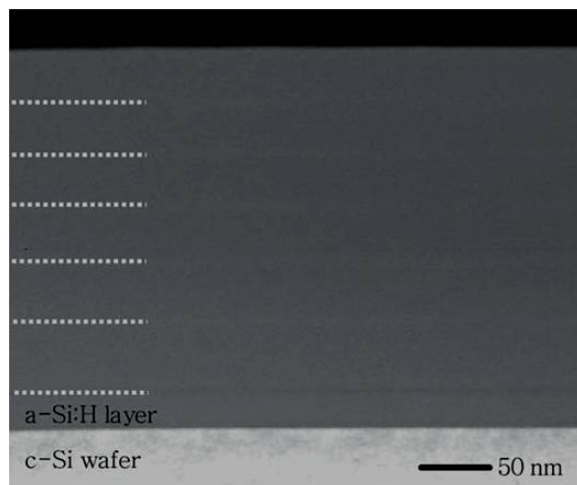


Figure 7.16: Cross-sectional TEM image of a 6-cycled pc-Si:H multilayer. Before the multilayer deposition, a 20 nm thick a-Si:H was deposited on a c-Si substrate. Adapted from S. W. Kwon, J. Kwak, S. Y. Myong, and K. S. Lim, *J. Non-Cryst. Solid*, 2006, **352**, 1132.

7.2.2.2 Bibliography

- D. L. Windt, F. E. Christensen, W. W. Craig, C. Hailey, F. A. Harrison, M. Jimenez-Garate, R. Kalyanaraman, and P. H. Mao, *J. Appl. Phys.*, 2000, **88**, 460.
- S. W. Kwon, J. Kwak, S. Y. Myong, and K. S. Lim, *J. Non-Cryst. Solid*, 2006, **352**, 1132.

7.2.3 TEM Imaging of Carbon Nanomaterials⁴

7.2.3.1 Introduction to TEM

Transmission electron microscopy (TEM) is a form of microscopy that uses an high energy electron beam (rather than optical light). A beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through. The image (formed from the interaction of the electrons with the sample) is magnified and focused onto an imaging device, such as a photographic film, a fluorescent screen, or detected by a CCD camera. In order to let the electrons pass through the specimen, the specimen has to be ultra thin, usually thinner than 10 nm.

The resolution of TEM is significantly higher than light microscopes. This is because the electron has a much smaller de Broglie wavelength than visible light (wavelength of 400~700 nm). Theoretically, the

⁴This content is available online at <<http://cnx.org/content/m22963/1.5/>>.

maximum resolution, d , has been limited by λ , the wavelength of the detecting source (light or electrons) and NA, the numerical aperture of the system.

$$d = \frac{\lambda}{2n \sin \alpha} \approx \frac{\lambda}{2NA} \quad (7.8)$$

For high speed electrons (in TEM, electron velocity is close to the speed of light, c , so that the special theory of relativity has to be considered), the λ_e :

$$\lambda_e = \frac{h}{\sqrt{(2m_0E(1 + E/2m_0c^2))}} \quad (7.9)$$

According to this formula, if we increase the energy of the detecting source, its wavelength will decrease, and we can get higher resolution. Today, the energy of electrons used can easily get to 200 keV, sometimes as high as 1 MeV, which means the resolution is good enough to investigate structure in sub-nanometer scale. Because the electrons is focused by several electrostatic and electromagnetic lenses, like the problems optical camera usually have, the image resolution is also limited by aberration, especially the spherical aberration called C_s . Equipped with a new generation of aberration correctors, transmission electron aberration-corrected microscope (TEAM) can overcome spherical aberration and get to half angstrom resolution.

Although TEAM can easily get to atomic resolution, the first TEM invented by Ruska in April 1932 could hardly compete with optical microscope, with only $3.6 \times 4.8 = 14.4$ magnification. The primary problem was the electron irradiation damage to sample in poor vacuum system. After World War II, Ruska resumed his work in developing high resolution TEM. Finally, this work brought him the Nobel Prize in physics 1986. Since then, the general structure of TEM hasn't changed too much as shown in Figure 7.17. The basic components in TEM are: electron gun, condenser system, objective lens (most important len in TEM which determines the final resolution), diffraction lens, projective lenses (all lens are inside the equipment column, between apertures), image recording system (used to be negative films, now is CCD cameras) and vacuum system.

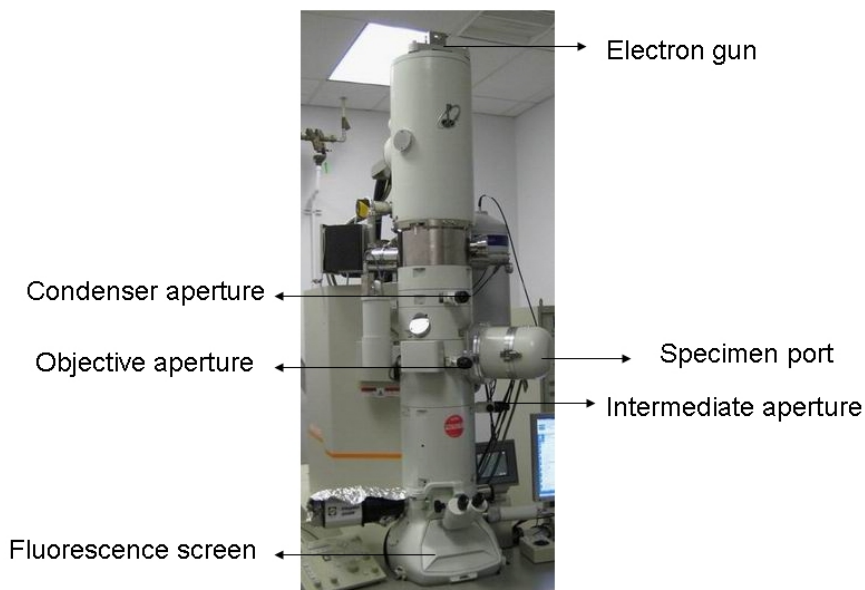


Figure 7.17: Position of the basic components in a TEM.

7.2.3.2 The family of carbon allotropes and carbon nanomaterials

Common carbon allotropes include diamond, graphite, amorphous C (a-C), fullerene (also known as buckyball), carbon nanotube (CNT, including single wall CNT and multi wall CNT), graphene. Most of them are chemically inert and have been found in nature. We can also define carbon as sp^2 carbon (which is graphite), sp^3 carbon (which is diamond) or hybrids of sp^2 and sp^3 carbon. As shown in Figure 7.18, (a) is the structure of diamond, (b) is the structure of graphite, (c) graphene is a single sheet of graphite, (d) is amorphous carbon, (e) is C_{60} , and (f) is single wall nanotube. As for carbon nanomaterials, fullerene, CNT and graphene are the three most well investigated, due to their unique properties in both mechanics and electronics. Under TEM, these carbon nanomaterials will display three different projected images.

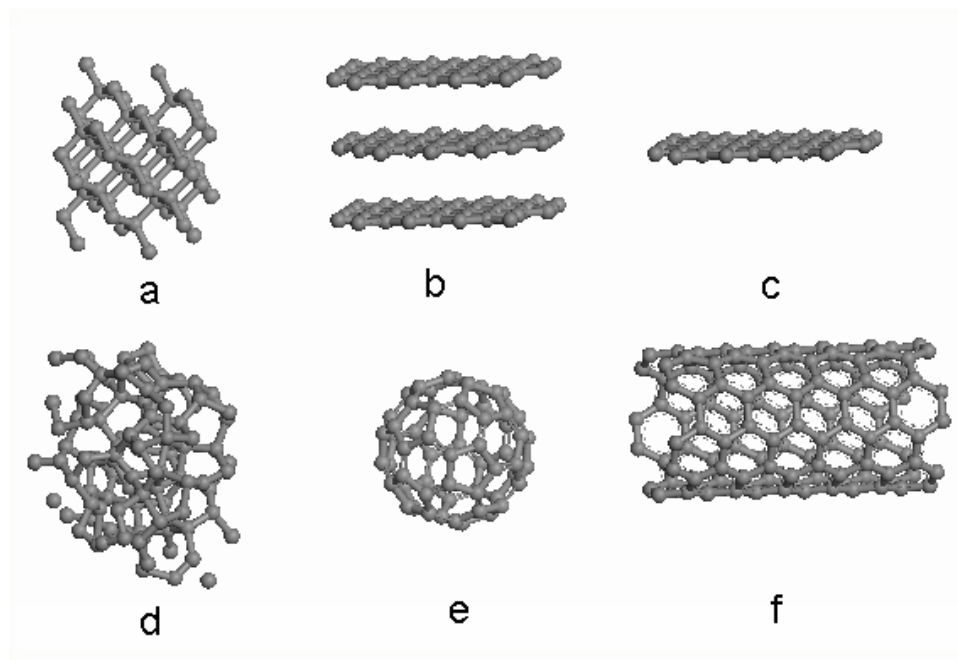


Figure 7.18: Six allotropes of carbon: a) diamond, b) graphite, c) graphene, d) amorphous carbon, e) C_{60} (Buckminsterfullerene or buckyball), f) single-wall carbon nanotube or buckytube.

7.2.3.3 Atomic structure of carbon nanomaterials under TEM

All carbon nanomaterials can be investigated under TEM. However, because of their difference in structure and shape, specific parts should be focused in order to obtain their atomic structure.

For C_{60} , which has a diameter of only 1 nm, it is relatively difficult to suspend a sample over a lacey carbon grid (a common kind of TEM grid usually used for nanoparticles). Even if the C_{60} sits on a thin a-C film, it also has some focus problems since the surface profile variation might be larger than 1 nm. One way to solve this problem is to encapsulate the C_{60} into single wall CNTs, which is known as nano peapods. This method has two benefits:

1. CNT helps focus on C_{60} . Single wall is aligned in a long distance (relative to C_{60}). Once it is suspended on lacey carbon film, it is much easier to focus on it. Therefore, the C_{60} inside can also be caught by minor focus changes.
2. The CNT can protect C_{60} from electron irradiation. Intense high energy electrons can permanently change the structure of the CNT. For C_{60} , which is more reactive than CNTs, it can not survive after exposing to high dose fast electrons.

In studying CNT cages, C_{92} is observed as a small circle inside the walls of the CNT. While a majority of electron energy is absorbed by the CNT, the sample is still not irradiation-proof. Thus, as is seen in Figure 7.19, after a 123 s exposure, defects can be generated and two C_{92} fused into one new larger fullerene.

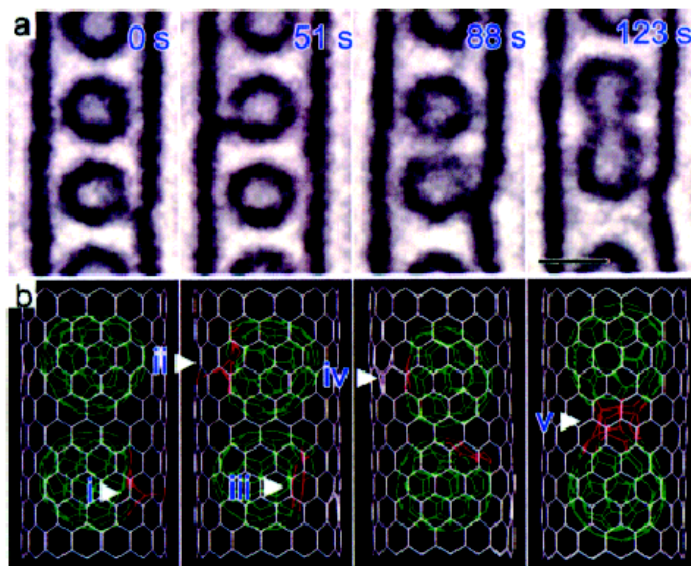


Figure 7.19: C₉₂ encapsulated in SWNTs under different electron irradiation time. Courtesy of Dr. Kazutomo SUENAGA, adapted from K. Urita, Y. Sato, K. Suenaga, A. Gloter, A. Hasimoto, M. Ishida, T. Shimada, T. Shinohara, S. Iijima, *Nano Lett.*, 2004, **4**, 2451. Copyright American Chemical Society (2004).

Although, the discovery of C₆₀ was first confirmed by mass spectra rather than TEM. When it came to the discovery of CNTs, mass spectra was no longer useful because CNTs shows no individual peak in mass spectra since any sample contains a range of CNTs with different lengths and diameters. On the other hand, HRTEM can provide a clear image evidence of their existence. An example is shown in Figure 7.20.

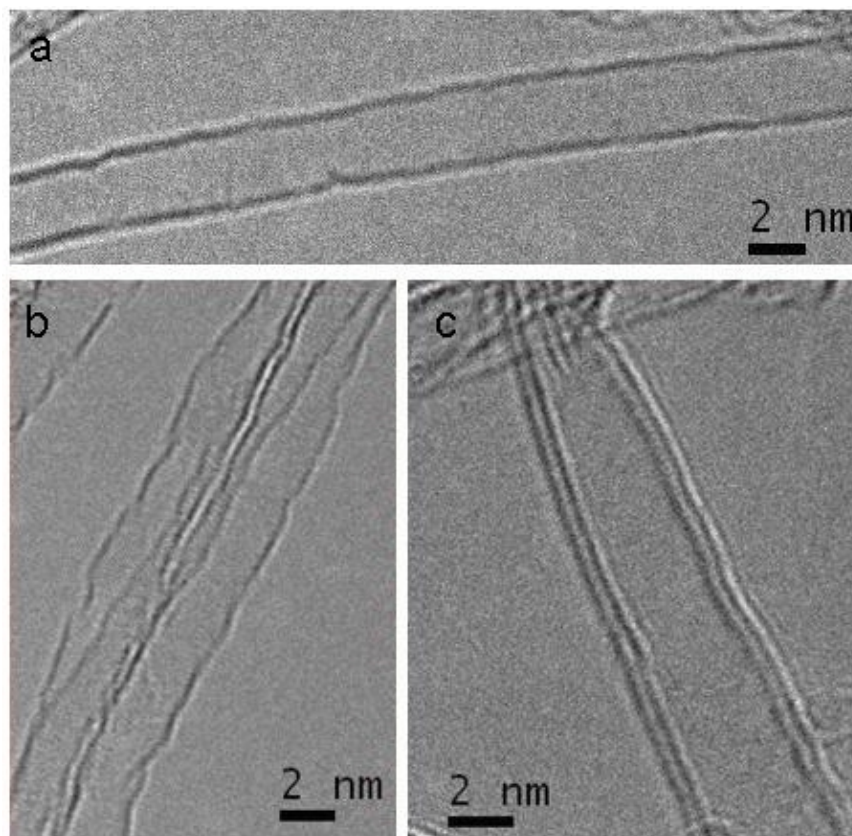


Figure 7.20: TEM images of SWNT and DWCNTs. Parallel dark lines corresponds to (002) lattice image of graphite. (a) and (b) SWNTs have 1 layer graphene sheet, diameter 3.2 nm. (c) DWCNT, diameter 4.0 nm.

Graphene is a planar fullerene sheet. Until recently, Raman, AFM and optical microscopy (graphene on 300 nm SiO₂ wafer) were the most convenient methods to characterize samples. However, in order to confirm graphene's atomic structure and determine the difference between mono-layer and bi-layer, TEM is still a good option. In Figure 7.21, a monolayer suspended graphene is observed with its atomic structure clearly shown. Inset is the FFT of the TEM image, which can be used as a filter to get an optimized structure image. High angle annular dark field (HAADF) image usually gives better contrast for different particles on it. It is also sensitive with changes of thickness, which allows a determination of the number of graphene layers.

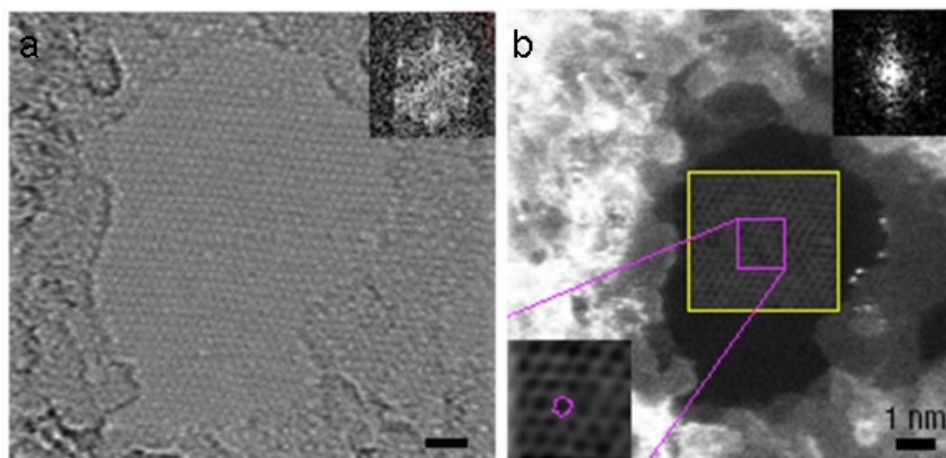


Figure 7.21: HRTEM of monolayer graphene. (a) Bright filed. (b) High Angle Annular Dark Field. Courtesy of Dr M. H. Gass, adapted from M. H. Gass, U. Bangert, A. L. Bleloch, P. Wang, R. R. Nair, and A. K. Geim, *Nature Nanotechnol.*, 2008, **3**, 676.

7.2.3.4 Graphene stacking and edges direction

Like the situation in CNT, TEM image is a projected image. Therefore, even with exact count of edge lines, it is not possible to conclude that a sample is a single layer graphene or multi-layer. If folding graphene has AA stacking (one layer is superposed on the other), with a projected direction of [001], one image could not tell the thickness of graphene. In order to distinguish such a bilayer of graphene from a single layer of graphene, a series of tilting experiment must be done. Different stacking structures of graphene are shown in Figure 7.22a.

Theoretically, graphene has the potential for interesting edge effects. Based upon its sp^2 structure, its edge can be either that of a zigzag or armchair configuration. Each of these possess different electronic properties similar to that observed for CNTs. For both research and potential application, it is important to control the growth or cutting of graphene with one specific edge. But before testing its electronic properties, all the edges have to be identified, either by directly imaging with STM or by TEM. Detailed information of graphene edges can be obtained with HRTEM, simulated with fast fourier transform (FFT). In Figure 7.22b, armchair directions are marked with red arrow respectively. A clear model in Figure 7.22c shows a 30 degree angle between zigzag edge and armchair edge.

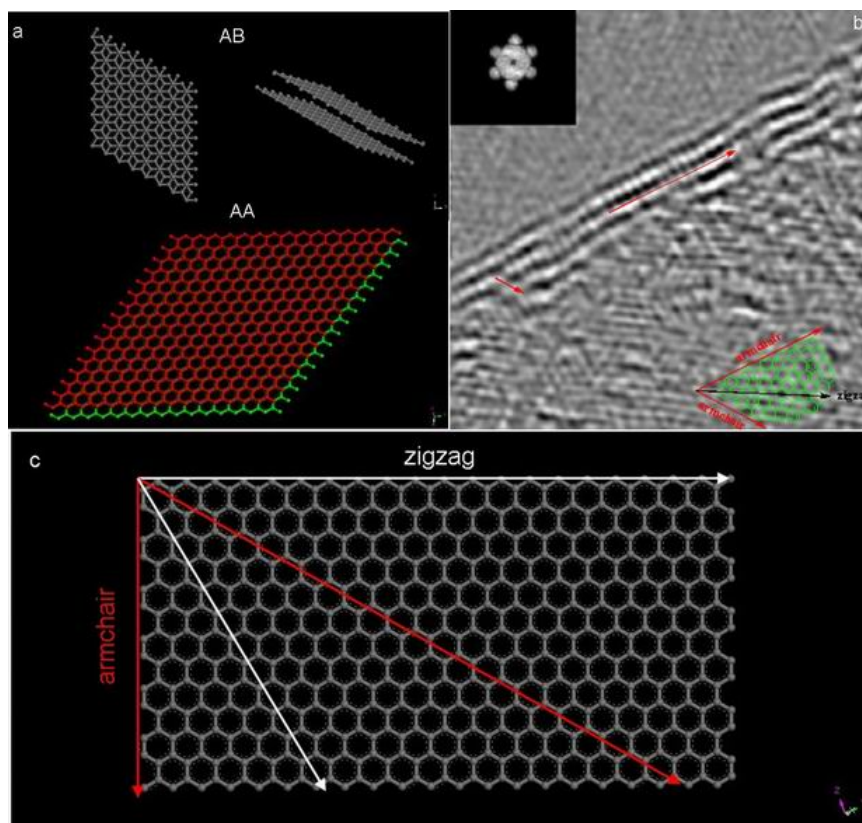


Figure 7.22: (a) Graphene stacking structure; (b) HRTEM image of graphene edges: zigzag and armchair (inset is FFT); (c) graphene edge model, a 30° angle between zigzag and armchair direction.

7.2.3.5 Bibliography

- K. Urita, Y. Sato, K. Suenaga, A. Gloter, A. Hasimoto, M. Ishida, T. Shimada, T. Shinohara, and S. Iijima, *Nano Lett.*, 2004, **4**, 2451.
- H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, *Nature*, 1985, **318**, 162.
- S. Iijima, *Nature*, 1991, **354**, 56.
- M. H. Gass, U. Bangert, A. L. Bleloch, P. Wang, R. R. Nair, and A. K. Geim, *Nature Nanotechnol.*, 2008, **3**, 676.
- L. Zheng and S. Iijima, *Phys. Rev. Lett.*, 2009, **102**, 015501.
- J. Campos-Delgado, J. M. Romo-Herrera, X. Jia, D. A. Cullen, H. Muramatsu, Y. A. Kim, T. Hayashi, Z. Ren, D. J. Smith, Y. Okuno, T. Ohba, H. Kanoh, K. Kaneko, M. Endo, H. Terrones, M. S. Dresselhaus, and M. Terrones, *Nano Lett.*, 2008, **8**, 2773.

7.3 Scanning Tunneling Microscopy

7.3.1 Scanning Tunneling Microscopy of Nanomaterials⁵

7.3.1.1 Introduction

Scanning tunneling microscopy (STM) is a powerful instrument that allows one to image the sample surface at the atomic level. As the first generation of scanning probe microscopy (SPM), STM paves the way for the study of nano-science and nano-materials. For the first time, researchers could obtain atom-resolution images of electrically conductive surfaces as well as their local electric structures. Because of this milestone invention, Gerd Binnig (Figure 7.23) and Heinrich Rohrer (Figure 7.24) won the Nobel Prize in Physics in 1986.



Figure 7.23: German physicist Gerd Binnig (1947 -).

⁵This content is available online at <<http://cnx.org/content/m38335/1.2/>>.

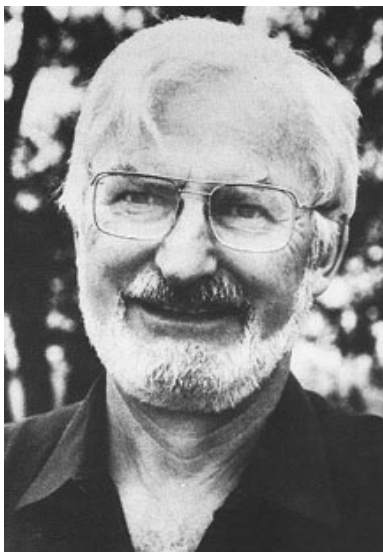


Figure 7.24: Swiss physicist Heinrich Rohrer (1933 -)

7.3.1.2 Principles of scanning tunneling microscopy

The key physical principle behind STM is the *tunneling effect*. In terms of their wave nature, the electrons in the surface atoms actually are not as tightly bonded to the nucleons as the electrons in the atoms of the bulk. More specifically, the electron density is not zero in the space outside the surface, though it will decrease exponentially as the distance between the electron and the surface increases (Figure 7.25a). So, when a metal tip approaches to a conductive surface within a very short distance, normally just a few Å, their perspective electron clouds will start to overlap, and generate tunneling current if a small voltage is applied between them, as shown in Figure 7.25b.

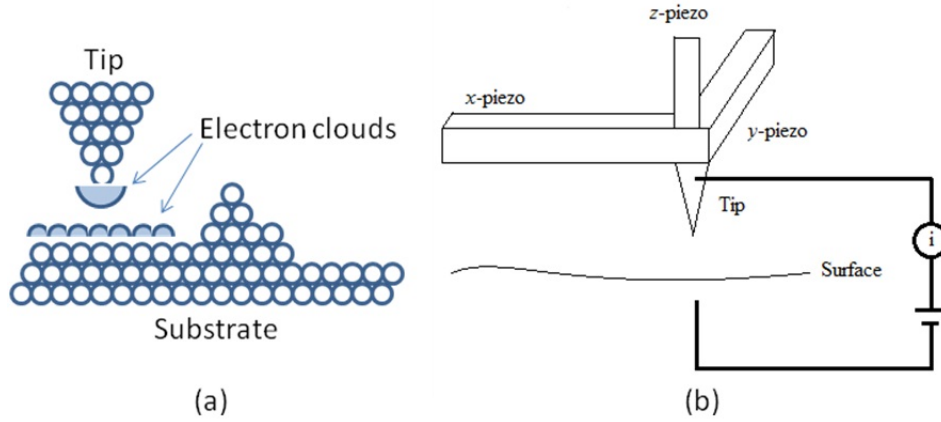


Figure 7.25: Schematic diagram of the principles of AFM showing (a) the interactions between tip and surface and (b) the tunneling current generated from tip and surface is measured and used as feedback to control the movement of the tip.

When we consider the separation between the tip and the surface as an ideal one-dimensional tunneling barrier, the tunneling probability, or the tunneling current I , will depend largely on s , the distance between the tip and surface, (7.10), where m is the electron mass, e the electron charge, h the Plank constant, $[U+03D5]$ the averaged work function of the tip and the sample, and V the bias voltage.

$$I \propto \exp(-2s [2m/h^2 (\langle\phi\rangle - e|V|/2)]^{1/2}) \quad (7.10)$$

A simple calculation will show us how strongly the tunneling current is affected by the distance (s). If s is increased by $\Delta s = 1 \text{ \AA}$, (7.11) and (7.12).

$$\Delta I = \exp(-2k_0 \Delta s) \quad (7.11)$$

$$k_0 = [2m/h^2 (\langle\phi\rangle - e|V|/2)]^{1/2} \quad (7.12)$$

Usually $(\langle\phi\rangle - e|V|/2)$ is about 5 eV, which k_0 about $1 \text{ \AA}^{-1}$, then $\Delta I/I = 1/s$. That means, if s changes by $1 \text{ \AA}$, the current will change by one order of the magnitude. That's the reason why we can get atom-level image by measuring the tunneling current between the tip and the sample.

In a typical STM operation process, the tip is scanning across the surface of sample in x-y plain, the instrument records the x-y position of the tip, measures the tunneling current, and control the height of the tip via a feedback circuit. The movements of the tip in x, y and z directions are all controlled by piezo ceramics, which can be elongated or shortened according to the voltage applied on them.

Normally, there are two modes of operation for STM, *constant height mode* and *constant current mode*. In constant height mode, the tip stays at a constant height when it scans through the sample, and the tunneling current is measured at different (x, y) position (Figure 7.25b). This mode can be applied when the surface of sample is very smooth. But, if the sample is rough, or has some large particles on the surface, the tip may contact with the sample and damage the surface. In this case, the constant current mode is applied. During this scanning process, the tunneling current, namely the distance between the tip and the sample, is settled to an unchanged target value. If the tunneling current is higher than that target value, that means

the height of the sample surface is increasing, the distance between the tip and sample is decreasing. In this situation, the feedback control system will respond quickly and retract the tip. Conversely, if the tunneling current drops below the target value, the feedback control will have the tip closer to the surface. According to the output signal from feedback control, the surface of the sample can be imaged.

7.3.1.3 Comparison of atomic force microscopy (AFM) and scanning tunneling microscopy (STM)

Both AFM and STM are widely used in nano-science. According to the different working principles though, they have their own advantages and disadvantages when measuring specific properties of sample (Table 7.1). STM requires an electric circuit including the tip and sample to let the tunneling current go through. That means, the sample for STM must be conducting. In case of AFM however, it just measures the deflection of the cantilever caused by the van der Waals forces between the tip and sample. Thus, in general any kind of sample can be used for AFM. But, because of the exponential relation of the tunneling current and distance, STM has a better resolution than AFM. In STM image one can actually “see” an individual atom, while in AFM it’s almost impossible, and the quality of AFM image is largely depended on the shape and contact force of the tip. In some cases, the measured signal would be rather complicated to interpret into morphology or other properties of sample. On the other side, STM can give straight forward electric property of the sample surface.

	AFM	STM
Sample requirement	-	Conducting
Work environment	Air, liquid	Vacuum
Lateral resolution	~ 1 nm	~ 0.1 nm
Vertical resolution	~ 0.05 nm	~ 0.05 nm
Working mode	Tapping, contact	Constant current, constant height

Table 7.1: Comparison of AFM and STM.

7.3.1.4 Applications of scanning tunneling microscopy in nanoscience.

STM provides a powerful method to detect the surface of conducting and semi-conducting materials. Recently STM can also be applied in the imaging of insulators, superlattice assemblies and even the manipulation of molecules on surface. More importantly, STM can provide the surface structure and electric property of surface at atomic resolution, a true breakthrough in the development of nano-science. In this sense, the data collected from STM could reflect the local properties even of single molecule and atom. With these valuable measurement data, one could give a deeper understanding of structure-property relations in nanomaterials.

An excellent example is the STM imaging of graphene on Ru(0001), as shown in Figure 7.26. Clearly seen is the superstructure with a periodicity of ~ 30 Å, coming from the lattice mismatch of 12 unit cells of the graphene and 11 unit cells of the underneath Ru(0001) substrate. This so-called moiré structure can also be seen in other systems when the adsorbed layers have strong chemical bonds within the layer and weak interaction with the underlying surface. In this case, the periodic superstructure seen in graphene tells us that the formed graphene is well crystallized and expected to have high quality.

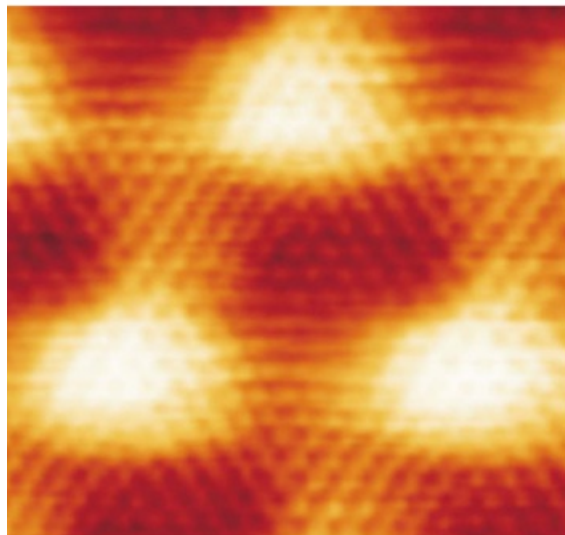


Figure 7.26: Atomically resolved image of the graphene overlayer. The scanning area is $40 \times 40 \text{ \AA}$, the operation mode is constant current mode, I_t is 1 nA , V_{Bias} is -0.05 V . Adapted with permission from S. Marchini, S. Gunther, and J. Wintterlin, *Phys. Rev. B*, 2007, **76**, 075429. Copyrighted by the American Physical Society.

Another good example is shown to see that the measurement from STM could tell us the bonding information in single-molecular level. In thiol- and thiophene-functionalization of single-wall carbon nanotubes (SWNTs) (Figure 7.27), the use of Au nanoparticles as chemical markers for AFM gives misleading results, while STM imaging could give correct information of substituent location. From AFM image, Au-thiol-SWNT (Figure 7.28a) shows that most of the sidewalls are unfunctionalized, while Au-thiophene-SWNT (Figure 7.28c) shows long bands of continuous functionalized regions on SWNT. This could lead to the estimation that thiophene is better functionalized to SWNT than thiol. Yet, if we look up to the STM image (Figure 7.28b and d), in thiol-SWNTs the multiple functional groups are tightly bonded in about $5 - 25 \text{ nm}$, while in thiophene-SWNTs the functionalization is spread out uniformly along the whole length of SWNT. This information indicates that actually the functionalization levels of thiol- and thiophene-SWNTs are comparable. The difference is that, in thiol-SWNTs, functional groups are grouped together and each group is bonded to a single gold nanoparticle, while in thiophene-SWNTs, every individual functional group is bonded to a nanoparticle.

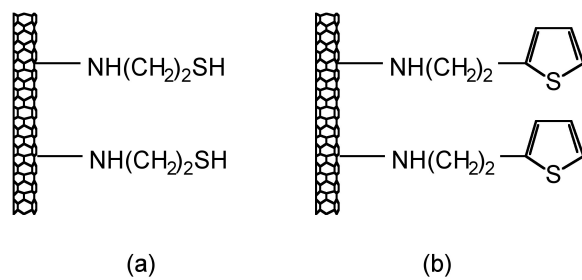


Figure 7.27: Structure of (a) thiol-functionalized SWNTs and thiophene-functionalized SWNTs.

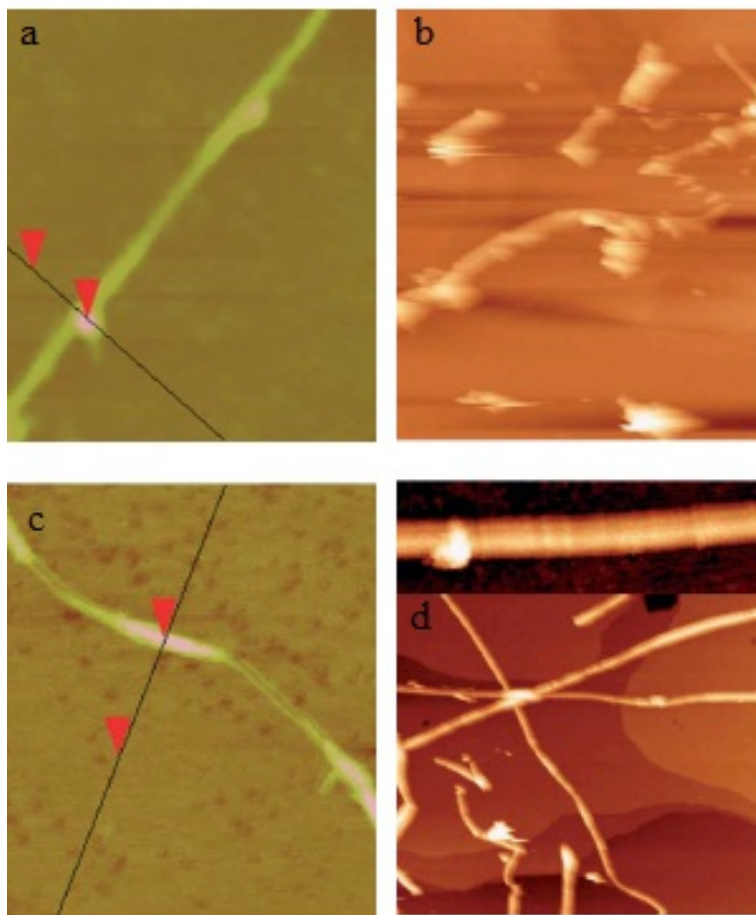


Figure 7.28: Difference between AFM and STM images of functionalized SWNTs. (a) and (c) are tapping mode AFM images and height profiles of thiol- and thiophene-SWNTs. (b) and (d) are STM images of thiol-SWNTs (scanning area is $4560 \times 4000 \text{ \AA}$, the operation mode is constant current mode, I_t is 3.25 pA , V_{Bias} is -0.5 V) and thiophene-SWNTs (scanning area is $4560 \times 4000 \text{ \AA}$, the operation mode is constant current mode, I_t is 5.66 pA , V_{Bias} is -0.8 V). Inset in (d) is a higher resolution image of the local defects on thiophene-SWNT ($500 \times 140 \text{ \AA}$, the operation mode is constant current mode, I_t is 25.5 pA , V_{Bias} is -0.8 V). Adapted from L. Zhang, J. Zhang, N. Schmandt, J. Cratty, V. N. Khabashesku, K. F. Kelly, and A. R. Barron, *Chem. Commun.*, 2005, 5429 (<http://dx.doi.org/10.1039/b509257d>)⁶. Reproduced by permission of The Royal Society of Chemistry.

7.3.1.5 Bibliography

- G. Binnig and H. Rohrer, *Surf. Sci.*, 1983, **126**, 236.
- G. Binnig and H. Rohrer, *Surf. Sci.*, 1985, **152/153**, 17.
- J. Griffith, *Annu. Rev. Mater. Sci.*, 1990, **20**, 219.

⁶<http://dx.doi.org/10.1039/b509257d>

- M. Poggi, L. Bottomley, and P. Lillehei, *Anal. Chem.*, 2002, **74**, 2851.
- P. Samori. *J. Mater. Chem.*, 2005, **14**, 1353.
- S. Marchini, S. Gunther, and J. Wintterlin, *Phys. Rev. B*, 2007, **76**, 075429.
- L. Zhang, J. Zhang, N. Schmandt, J. Cratty, V. N. Khabashesku, K. F. Kelly, and A. R. Barron, *Chem. Commun.*, 2005, 5429.

7.3.2 Adaptations to Scanning Tunneling Microscopy⁷

7.3.2.1 Introduction

Scanning tunneling microscopy (STM) is a relatively recent imaging technology that has proven very useful for determining the topography of conducting and semiconducting samples with angstrom ($\text{\AA}$) level precision. STM was invented by Gerd Binnig (Figure 7.29) and Heinrich Rohrer (Figure 7.30), who both won the 1986 Nobel Prize in physics for their technological advances.



Figure 7.29: German physicist Gerd Binnig (1947 -).

⁷This content is available online at <<http://cnx.org/content/m43549/1.1/>>.

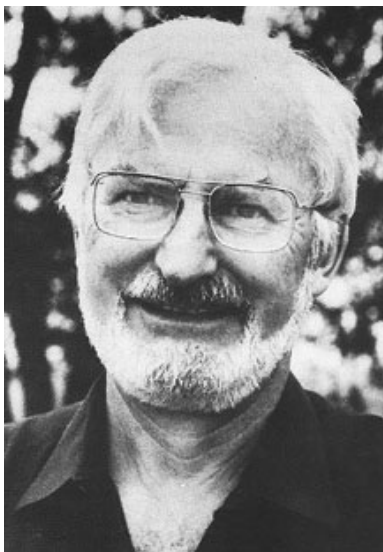


Figure 7.30: Swiss physicist Heinrich Rohrer (1933 -).

The main component of a scanning tunneling microscope is a rigid metallic probe tip, typically composed of tungsten, connected to a piezodrive containing three perpendicular piezoelectric transducers (Figure 7.31). The tip is brought within a fraction of a nanometer of an electrically conducting sample. At close distances, the electron clouds of the metal tip overlap with the electron clouds of the surface atoms (Figure 7.31 inset). If a small voltage is applied between the tip and the sample a tunneling current is generated. The magnitude of this tunneling current is dependent on the bias voltage applied and the distance between the tip and the surface. A current amplifier can convert the generated tunneling current into a voltage. The magnitude of the resulting voltage as compared to the initial voltage can then be used to control the piezodrive, which controls the distance between the tip and the surface (i.e., the z direction). By scanning the tip in the x and y directions, the tunneling current can be measured across the entire sample. The STM system can operate in either of two modes: .

1. Constant height.
2. Constant current.

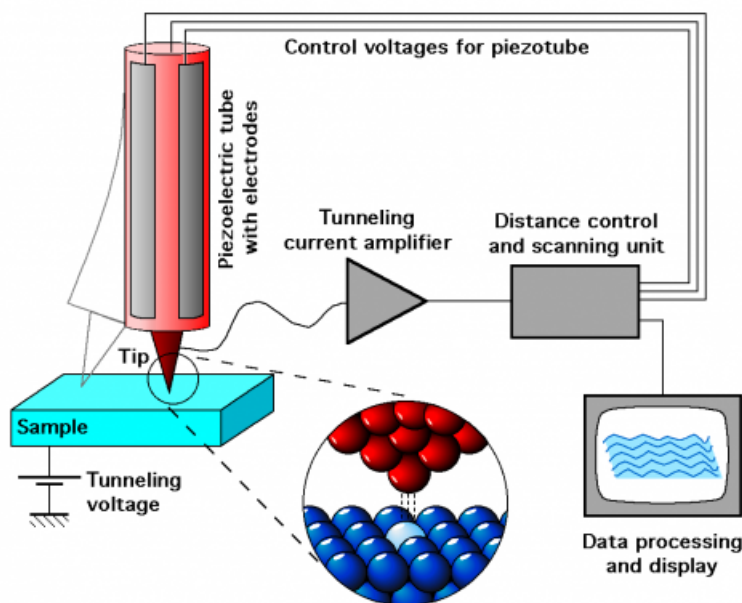


Figure 7.31: Schematic drawing of a STM apparatus.

In constant height mode, the tip is fixed in the z direction and the change in tunneling current as the tip changes in the x,y direction is collected and plotted to describe the change in topography of the sample. This method is dangerous for use in samples with fluctuations in height as the fixed tip might contact and destroy raised areas of the sample. A common method for non-uniformly smooth samples is constant current mode. In this mode, a target current value, called the set point, is selected and the tunneling current data gathered from the sample is compared to the target value. If the collected voltage deviates from the set point, the tip is moved in the z direction and the voltage is measured again until the target voltage is reached. The change in the z direction required to reach the set point is recorded across the entire sample and plotted as a representation of the topography of the sample. The height data is typically displayed as a gray scale image of the topography of the sample, where lighter areas typically indicate raised sample areas and darker spots indicate protrusions. These images are typically colored for better contrast.

The standard method of STM, described above, is useful for many substances (including high precision optical components, disk drive surfaces, and buckyballs) and is typically used under ultrahigh vacuum to avoid contamination of the samples from the surrounding systems. Other sample types, such as semiconductor interfaces or biological samples, need some enhancements to the traditional STM apparatus to yield more detailed sample information. Three such modifications, spin-polarized STM (SP-STM), ballistic electron emission microscopy (BEEM) and photon STM (PSTM) are summarized in Table 7.2 and in described in detail below.

Name	Alterations to conventional STM	Sample types	Limitations
STM	None	Conducting surface	Rigidity of probe
SP-STM	Magnetized STM tip	Magnetic	Needs to be overlaid with STM, magnetized tip type
BEEM	Three-terminal with base electrode and current collector	Interfaces	Voltage, changes due to barrier height
PSTM	Optical fiber tip	Biological	Optical tip and prism manufacture

Table 7.2: Comparison of conventional STM and alterations.

7.3.2.2 Spin-polarized STM

Spin-polarized scanning tunneling microscopy (SP-STM) can be used to provide detailed information of magnetic phenomena on the single-atom scale. This imaging technique is particularly important for accurate measurement of superconductivity and high-density magnetic data storage devices. In addition, SP-STM, while sensitive to the partial magnetic moments of the sample, is not a field-sensitive technique and so can be applied in a variety of different magnetic fields.

7.3.2.2.1 Device setup and sample preparation

In SP-STM, the STM tip is coated with a thin layer of magnetic material. As with STM, voltage is then applied between tip and sample resulting in tunneling current. Atoms with partial magnetic moments that are aligned in the same direction as the partial magnetic moment of the atom at the very tip of the STM tip show a higher magnitude of tunneling current due to the interactions between the magnetic moments. Likewise, atoms with partial magnetic moments opposite that of the atom at the tip of the STM tip demonstrate a reduced tunneling current (Figure 7.32). A computer program can then translate the change in tunneling current to a topographical map, showing the spin density on the surface of the sample.

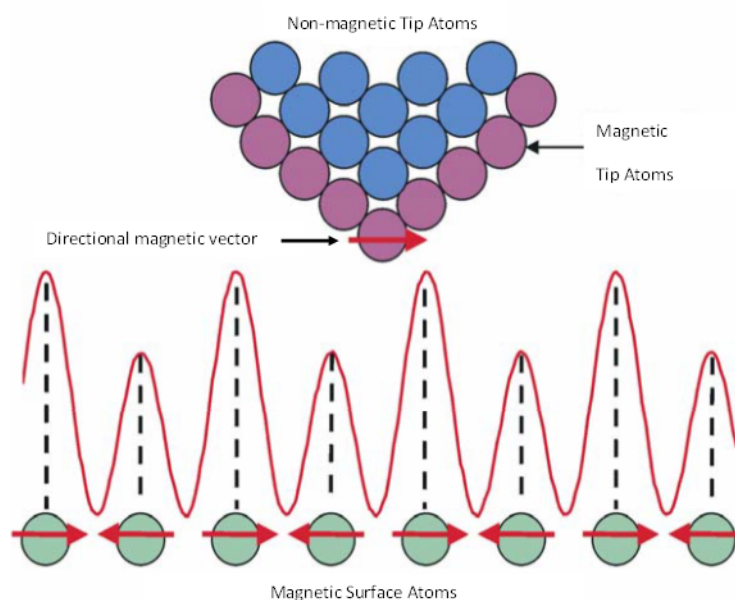


Figure 7.32: Schematic illustration of magnetized tip for SP-STM.

The sensitivity to magnetic moments depends greatly upon the direction of the magnetic moment of the tip, which can be controlled by the magnetic properties of the material used to coat the outermost layer of the tungsten STM probe. A wide variety of magnetic materials have been studied as possible coatings, including both ferromagnetic materials, such as a thin coat of iron or of gadolinium, and antiferromagnetic materials such as chromium. Another method that has been used to make a magnetically sensitive probe tip is irradiation of a semiconducting GaAs tip with high energy circularly polarized light. This irradiation causes a splitting of electrons in the GaAs valence band and population of the conduction band with spin-polarized electrons. These spin-polarized electrons then provide partial magnetic moments which in turn influence the tunneling current generated by the sample surface.

Sample preparation for SP-STM is essentially the same as for STM. SP-STM has been used to image samples such as thin films and nanoparticle constructs as well as determining the magnetic topography of thin metallic sheets such as in Figure 7.33. The upper image is a traditional STM image of a thin layer of cobalt, which shows the topography of the sample. The second image is an SP-STM image of the same layer of cobalt, which shows the magnetic domain of the sample. The two images, when combined provide useful information about the exact location of the partial magnetic moments within the sample.

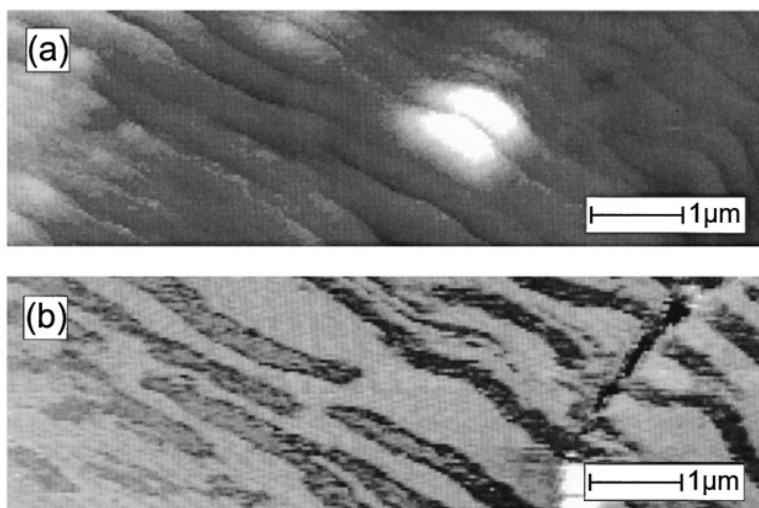


Figure 7.33: A thin layer of Co(0001) as imaged by (a) STM, showing the topography, and (b) SP-STM, showing the magnetic domain structure. Image adapted from W. Wulfhekel and J. Kirschner, *Appl. Phys. Lett.*, 1999, **75**, 1944.

7.3.2.2.2 Limitations

One of the major limitations with SP-STM is that both distance and partial magnetic moment yield the same contrast in a SP-STM image. This can be corrected by combination with conventional STM to get multi-domain structures and/or topological information which can then be overlaid on top of the SP-STM image, correcting for differences in sample height as opposed to magnetization.

The properties of the magnetic tip dictate much of the properties of the technique itself. If the outermost atom of the tip is not properly magnetized, the technique will yield no more information than a traditional STM. The direction of the magnetization vector of the tip is also of great importance. If the magnetization vector of the tip is perpendicular to the magnetization vector of the sample, there will be no spin contrast. It is therefore important to carefully choose the coating applied to the tungsten STM tip in order to align appropriately with the expected magnetic moments of the sample. Also, the coating makes the magnetic tips more expensive to produce than standard STM tips. In addition, these tips are often made of mechanically soft materials, causing them to wear quickly and require a high cost of maintenance.

7.3.2.3 Ballistic electron emission microscopy

Ballistic electron emission microscopy (BEEM) is a technique commonly used to image semiconductor interfaces. Conventional surface probe techniques can provide detailed information on the formation of interfaces, but lack the ability to study fully formed interfaces due to inaccessibility to the surface. BEEM allows for the ability to obtain a quantitative measure of electron transport across fully formed interfaces, something necessary for many industrial applications.

7.3.2.3.1 Device setup and sample preparation

BEEM utilizes STM with a three-electrode configuration, as seen in Figure 7.31. In this technique, ballistic electrons are first injected from a STM tip into the sample, traditionally composed of at least two layers

separated by an interface, which rests on three indium contact pads that provide a connection to a base electrode (Figure 7.34). As the voltage is applied to the sample, electrons tunnel across the vacuum and through the first layer of the sample, reaching the interface, and then scatter. Depending on the magnitude of the voltage, some percentage of the electrons tunnel through the interface, and can be collected and measured as a current at a collector attached to the other side of the sample. The voltage from the STM tip is then varied, allowing for measurement of the barrier height. The barrier height is defined as the threshold at which electrons will cross the interface and are measurable as a current in the far collector. At a metal/n-type semiconductor interface this is the difference between the conduction band minimum and the Fermi level. At a metal/p-type semiconductor interface this is the difference between the valence band maximum of the semiconductor and the metal Fermi level. If the voltage is less than the barrier height, no electrons will cross the interface and the collector will read zero. If the voltage is greater than the barrier height, useful information can be gathered about the magnitude of the current at the collector as opposed to the initial voltage.

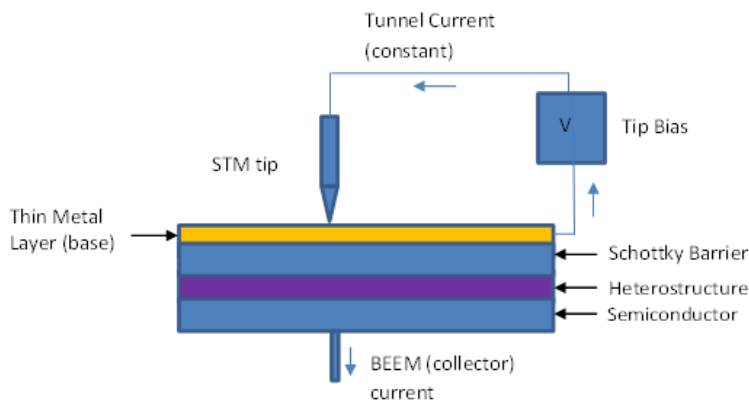


Figure 7.34: Diagram of a STM/BEEM system. The tip is maintained at the tunneling voltage, V , and the tunneling current, $I_t = V_t/R_F$, is held constant by the STM feedback circuit. The sample base layer is grounded and current into the semiconductor is measured by a virtual ground current amplifier.

Samples are prepared from semiconductor wafers by chemical oxide growth-strip cycles, ending with the growth of a protective oxide layer. Immediately prior to imaging the sample is spin-etched in an inert environment to remove oxides of oxides and then transferred directly to the ultra-high vacuum without air exposure. The BEEM apparatus itself is operated in a glove box under inert atmosphere and shielded from light.

Nearly any type of semiconductor interface can be imaged with BEEM. This includes both simple binary interfaces such as Au/n-Si(100) and more chemically complex interfaces such as Au/n-GaAs(100), such as seen in Figure 7.35.

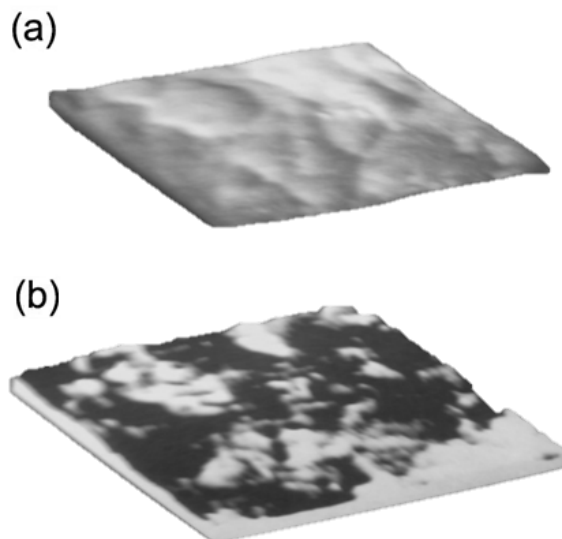


Figure 7.35: Images of Au/n-GaAs(100) layer (image area $510 \text{ \AA} \times 390 \text{ \AA}$) showing (a) the topography of the Au surface and (b) the BEEM grey-scale interface image. Image adapted from M. H. Hecht, L. D. Bell, W. J. Kaiser, and F. J. Grunthaner, *Appl. Phys. Lett.*, 1989, **55**, 780.

7.3.2.3.2 Limitations

Expected barrier height matters a great deal in the desired setup of the BEEM apparatus. If it is necessary to measure small collector currents, such as with an interface of high-barrier-height, a high-gain, low-noise current preamplifier can be added to the system. If the interface is of low-barrier-height, the BEEM apparatus can be operated at very low temperatures, accomplished by immersion of the STM tip in liquid nitrogen and enclosure of the BEEM apparatus in a nitrogen-purged glove box.

7.3.2.4 Photon STM

Photon scanning tunneling microscopy (PSTM) measures light to determine more information about characteristic sample topography. It has primarily been used as a technique to measure the electromagnetic interaction of two metallic objects in close proximity to one another and biological samples, which are both difficult to measure using many other common surface analysis techniques.

7.3.2.4.1 Device setup and sample preparation

This technique works by measuring the tunneling of photons to an optical tip. The source of these photons is the evanescent field generated by the total internal reflection (TIR) of a light beam from the surface of the sample (Figure 7.36). This field is characteristic of the sample material on the TIR surface, and can be measured by a sharpened optical fiber probe tip where the light intensity is converted to an electrical signal (Figure 7.37). Much like conventional STM, the force of this electrical signal modifies the location of the tip in relation to the sample. By mapping these modifications across the entire sample, the topography can be

determined to a very accurate degree as well as allowing for calculations of polarization, emission direction and emission time.

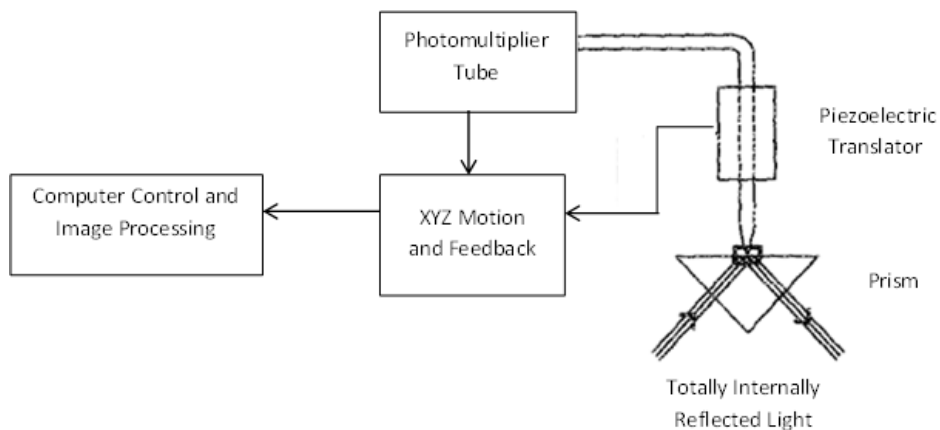


Figure 7.36: A schematic of a PSTM system.

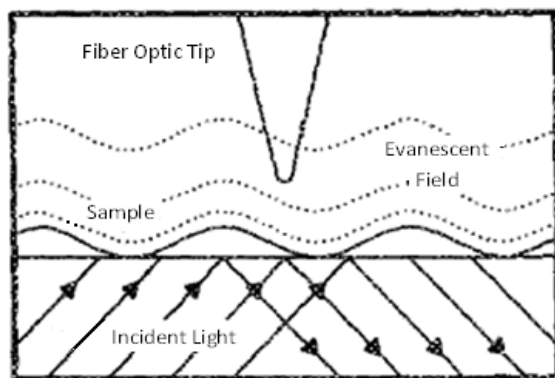


Figure 7.37: A TIR light beam generates an evanescent field which is modulated by the sample. A sharpened fiber optic probe tip receives light from the evanescent field and spatial variations in evanescent field intensity form the basis for imaging.

In PSTM, the vertical resolution is governed only by the noise, as opposed to conventional STM where the vertical resolution is limited by the tip dimensions. Therefore, this technique provides advantages over more conventional STM apparatus for samples where subwavelength resolution in the vertical dimension is a critical measurement, including fractal metal colloid clusters, nanostructured materials and simple organic

molecules.

Samples are prepared by placement on a quartz or glass slide coupled to the TIR face of a triangular prism containing a laser beam, making the sample surface into the TIR surface (Figure 7.37). The optical fiber probe tips are constructed from UV grade quartz optical fibers by etching in HF acid to have nominal end diameters of 200 nm or less and resemble either a truncated cone or a paraboloid of revolution (Figure 7.38).

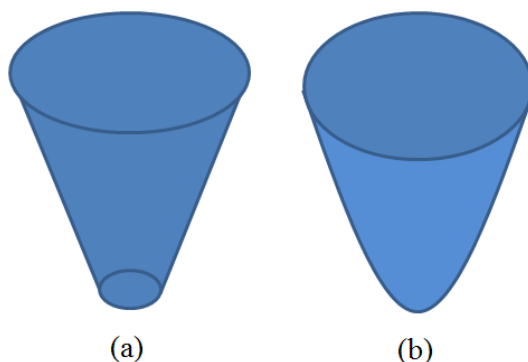


Figure 7.38: Possible optical fiber tip configurations: (a) truncated cone and (b) paraboloid of rotation.

PSTM shows much promise in the imaging of biological materials due to the increase in vertical resolution and the ability to measure a sample within a liquid environment with a high index TIR substrate and probe tip. This would provide much more detailed information about small organisms than is currently available.

7.3.2.4.2 Limitations

The majority of the limitations in this technique come from the materials and construction of the optical fibers and the prism used in the sample collection. The sample needs to be kept at low temperatures, typically around 100K, for the duration of the imaging and therefore cannot decompose or be otherwise negatively impacted by drastic temperature changes.

7.3.2.5 Conclusion

Scanning tunneling microscopy can provide a great deal of information into the topography of a sample when used without adaptations, but with adaptations, the information gained is nearly limitless. Depending on the likely properties of your sample surface, SP-STM, BEEM and PSTM can provide much more accurate topographical pictures than conventional forms of STM (Table 7.2). All of these adaptations to STM have their limitations and all work within relatively specialized categories and subsets of substances, but they are very strong tools that are constantly improving to provide more useful information about materials to the nanometer scale.

7.3.2.6 Bibliography

- R. Berndt and J. K. Gimzewski, *Phys. Rev. B*, 1993, **48**, 4746.
- G. Binnig, H. Rohrer, C. Gerber, and E. Weibel, *Phys. Rev. Lett.*, 1982, **49**, 57.
- M. Bode, *Rep. Prog. Phys.* 2003, **66**, 523.
- M. H. Hecht, L. D. Bell, W. J. Kaiser, and F. J. Grunthaner, *Appl. Phys. Lett.*, 1989, **55**, 780.

- W. J. Kaiser and L. D. Bell, *Phys. Rev. Lett.*, 1988, **60**, 1406.
- R. C. Reddick, D. W. Warmack, D. W. Chilcott, S. L. Sharp, and T. L. Ferrell, *Rev. Sci. Instrum.*, 1990, **61**, 3669.
- D. P. Tsai, J. Kovacs, Z. Wang, M. Moskovits, V. M. Shalaev, J. S. Suh, and R. Botet, *Phys. Rev. Lett.*, 1994, **72**, 4149.
- W. Wulfhekel and J. Kirschner, *Appl. Phys. Lett.*, 1999, **75**, 1944.

7.4 Spectroscopic Characterization of Nanoparticles

7.4.1 Using UV-vis for the detection and characterization of silicon quantum dots⁸

7.4.1.1 What are quantum dots?

Quantum dots (QDs) are small semiconductor nanoparticles generally composed of two elements that have extremely high quantum efficiencies when light is shined on them. The most common quantum dots are CdSe, PbS, and ZnSe, but there are many many other varieties of these particles that contain other elements as well. QDs can also be made of just three elements or just one element such as silicon.

7.4.1.2 Synthesis of silicon quantum dots

Silicon quantum dots are synthesized in inverse micelles. SiCl_4 is reduced using a two fold excess of LiAlH_4 (Figure 7.39). After the silicon has been fully reduced and the excess reducing agent quenched, the particles are capped with hydrogens and are hydrophobic. A platinum catalyzed ligand exchange of hydrogen for allylamine will produce hydrophilic particles (Figure 7.40). All reactions in making these particles are extremely air sensitive, and silica is formed readily, so the reactions should be performed in a highly controlled atmosphere, such as a glove box. The particles are then washed in DMF, and finally filtered and stored in deionized water. This will allow the Si QDs to be pure in water, and the particles are ready for analysis. This technique yields Si QDs of 1 - 2 nm in size.

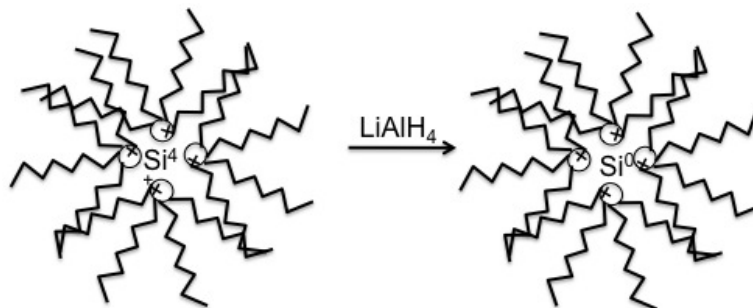


Figure 7.39: A schematic representation of the inverse micelle used for the synthesis of Si QDs.

⁸This content is available online at <<http://cnx.org/content/m34655/1.1/>>.

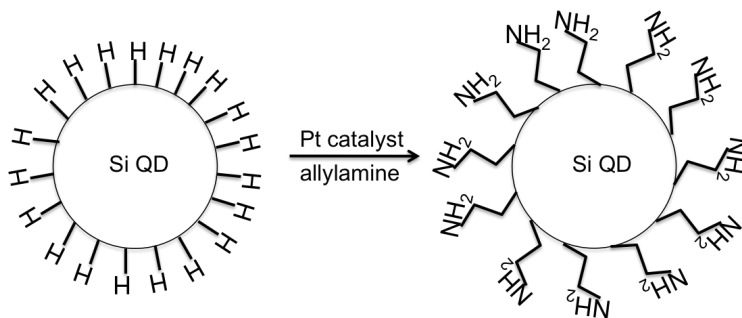


Figure 7.40: Conversion of hydrophobic Si QDs to hydrophilic Si QDs. Adapted from J. H. Warner, A. Hoshino, K. Yamamoto, and R. D. Tilley, *Angew. Chem., Int. Ed.*, 2005, **44**, 4550. Copyright: American Chemical Society (2005).

7.4.1.2.1 Sample preparation of Si QDs

The reported absorption wavelength for 1 - 2 nm Si QDs is 300 nm. With the hydrophobic Si QDs, UV-vis absorbance analysis in toluene does not yield an acceptable spectrum because the UV-vis absorbance cutoff is 287 nm, which is very close to 300 nm for the peaks to be resolvable. A better hydrophobic solvent would be hexanes. All measurements of these particles would require a quartz cuvette since the glass absorbance cutoff (300 nm) is exactly where the particles would be observed. Hydrophilic substituted particles do not need to be transferred to another solvent because water's absorbance cutoff is much lower. There is usually a slight impurity of DMF in the water due to residue on the particles after drying. If there is a DMF peak in the spectrum with the Si QDs the wavelengths are far enough apart to be resolved.

7.4.1.3 What information can be obtained from UV-visible spectra?

Quantum dots are especially interesting when it comes to UV-vis spectroscopy because the size of the quantum dot can be determined from the position of the absorption peak in the UV-vis spectrum. Quantum dots absorb different wavelengths depending on the size of the particles (e.g., Figure 7.41). Many calibration curves would need to be done to determine the exact size and concentration of the quantum dots, but it is entirely possible and very useful to be able to determine size and concentration of quantum dots in this way since other ways of determining size are much more expensive and extensive (electron microscopy is most widely used for this data).

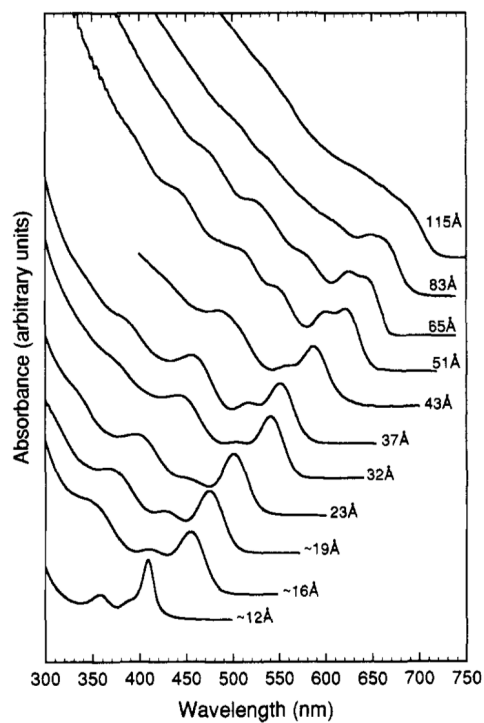


Figure 7.41: Absorbance of different sized CdSe QDs. Reprinted with permission from C. B. Murray, D. J. Norris, and M. G. Bawendi, *J. Am. Chem. Soc.*, 1993, **115**, 8706. Copyright: American Chemical Society (1993).

An example of silicon quantum dot data can be seen in Figure 7.42. The wider the absorbance peak is, the less monodispersed the sample is.

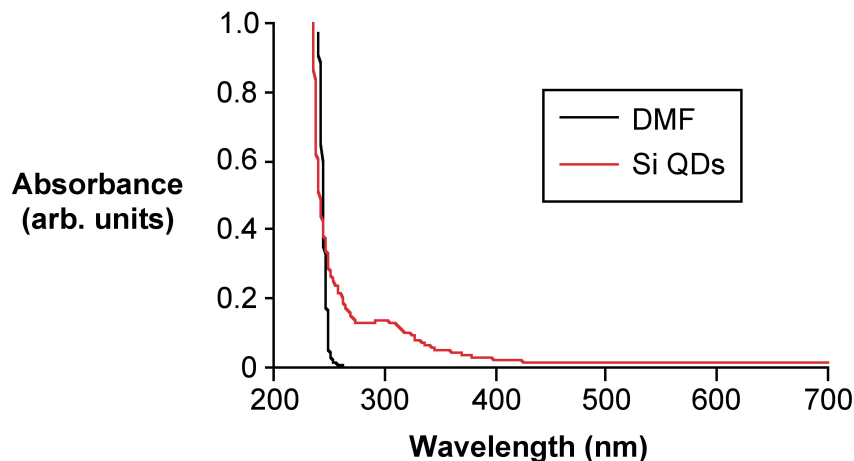


Figure 7.42: UV-vis absorbance spectrum of 1 - 2 nm Si QDs with a DMF reference spectrum.

7.4.1.3.1 Why is knowing the size of QDs important?

Different size (different excitation) quantum dots can be used for different applications. The absorbance of the QDs can also reveal how monodispersed the sample is; more monodispersity in a sample is better and more useful in future applications. Silicon quantum dots in particular are currently being researched for making more efficient solar cells. The monodispersity of these quantum dots is particularly important for getting optimal absorbance of photons from the sun or other light source. Different sized quantum dots will absorb light differently, and a more exact energy absorption is important in the efficiency of solar cells. UV-vis absorbance is a quick, easy, and cheap way to determine the monodispersity of the silicon quantum dot sample. The peak width of the absorbance data can give that information. The other important information for future applications is to get an idea about the size of the quantum dots. Different size QDs absorb at different wavelengths; therefore, specific size Si QDs will be required for different cells in tandem solar cells.

7.4.1.4 Bibliography

- J. H. Warner, A. Hoshino, K. Yamamoto, and R. D. Tilley, *Angew. Chem., Int. Ed.*, 2005, **44**, 4550.
- C. B. Murray, D. J. Norris, and M. G. Bawendi, *J. Am. Chem. Soc.*, 1993, **115**, 8706.

7.4.2 Optical Properties of Group 12-16 (II-VI) Semiconductor Nanoparticles⁹

7.4.2.1 What are Group 12-16 semiconductors?

Semiconductor materials are generally classified on the basis of the periodic table group that their constituent elements belong to. Thus, Group 12-16 semiconductors, formerly called II-VI semiconductors, are materials whose cations are from the Group 12 and anions are from Group 16 in the periodic table (Figure 7.43). Some examples of Group 12-16 semiconductor materials are cadmium selenide (CdSe), zinc sulfide (ZnS), cadmium telluride (CdTe), zinc oxide (ZnO), and mercuric selenide (HgSe) among others.

⁹This content is available online at <<http://cnx.org/content/m34553/1.1/>>.

NOTE: The new IUPAC (International Union of Pure and Applied Chemistry) convention is being followed in this document, to avoid any confusion with regard to conventions used earlier. In the old IUPAC convention, Group 12 was known as Group IIB with the roman numeral 'II' referring to the number of electrons in the outer electronic shells and B referring to being on the right part of the table. However, in the CAS (Chemical Abstracts Service), the alphabet B refers to transition elements as compared to main group elements, though the roman numeral has the same meaning. Similarly, Group 16 was earlier known as Group VI because all the elements in this group have 6 valence shell electrons.

Group →	12	13	14	15	16
↓ Period					
2		5 B	6 C	7 N	8 O
3		13 Al	14 Si	15 P	16 S
4	30 Zn	31 Ga	32 Ge	33 As	34 Se
5	48 Cd	49 In	50 Sn	51 Sb	52 Te
6	80 Hg	81 Tl	82 Pb	83 Bi	84 Po
7	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh

Figure 7.43: The red box indicates the Group 12 and Group 16 elements in the periodic table.

7.4.2.2 What are Group 12-16 (II-VI) semiconductor nanoparticles?

From the Greek word *nanos* - meaning "dwarf" this prefix is used in the metric system to mean 10^{-9} or one billionth ($1/1,000,000,000$). Thus a nanometer is 10^{-9} or one billionth of a meter, and a nanojoule is 10^{-9} or one billionth of a Joule, etc. A nanoparticle is ordinarily defined as any particle with at least one of its dimensions in the 1 - 100 nm range.

Nanoscale materials often show behavior which is intermediate between that of a bulk solid and that of an individual molecule or atom. An inorganic nanocrystal can be imagined to be comprised of a few atoms or molecules. It thus will behave differently from a single atom; however, it is still smaller than a macroscopic solid, and hence will show different properties. For example, if one would compare the chemical reactivity of a bulk solid and a nanoparticle, the latter would have a higher reactivity due to a significant fraction of the total number of atoms being on the surface of the particle. Properties such as boiling point, melting point, optical properties, chemical stability, electronic properties, etc. are all different in a nanoparticle as compared to its bulk counterpart. In the case of Group 12-16 semiconductors, this reduction in size from bulk to the nanoscale results in many size dependent properties such as varying band gap energy, optical and electronic properties.

7.4.2.3 Optical properties of semiconductor quantum nanoparticles

In the case of semiconductor nanocrystals, the effect of the size on the optical properties of the particles is very interesting. Consider a Group 12-16 semiconductor, cadmium selenide (CdSe). A 2 nm sized CdSe

crystal has a blue color fluorescence whereas a larger nanocrystal of CdSe of about 6 nm has a dark red fluorescence (Figure 7.44). In order to understand the size dependent optical properties of semiconductor nanoparticles, it is important to know the physics behind what is happening at the nano level.



Figure 7.44: Fluorescing CdSe quantum dots synthesized in a heat transfer liquid of different sizes (M. S. Wong, Rice University).

7.4.2.3.1 Energy levels in a semiconductor

The electronic structure of any material is given by a solution of Schrödinger equations with boundary conditions, depending on the physical situation. The electronic structure of a semiconductor (Figure 7.45) can be described by the following terms:

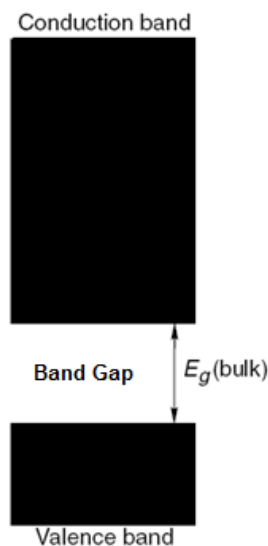


Figure 7.45: Simplified representation of the energy levels in a bulk semiconductor.

7.4.2.3.1.1 Energy level

By the solution of Schrödinger's equations, the electrons in a semiconductor can have only certain allowable energies, which are associated with energy levels. No electrons can exist in between these levels, or in other words can have energies in between the allowed energies. In addition, from Pauli's Exclusion Principle, only 2 electrons with opposite spin can exist at any one energy level. Thus, the electrons start filling from the lowest energy levels. Greater the number of atoms in a crystal, the difference in allowable energies become very small, thus the distance between energy levels decreases. However, this distance can never be zero. For a bulk semiconductor, due to the large number of atoms, the distance between energy levels is very small and for all practical purpose the energy levels can be described as continuous (Figure 7.45).

7.4.2.3.1.2 Band gap

From the solution of Schrödinger's equations, there are a set of energies which is not allowable, and thus no energy levels can exist in this region. This region is called the band gap and is a quantum mechanical phenomenon (Figure 7.45). In a bulk semiconductor the bandgap is fixed; whereas in a quantum dot nanoparticle the bandgap varies with the size of the nanoparticle.

7.4.2.3.1.3 Valence band

In bulk semiconductors, since the energy levels can be considered as continuous, they are also termed as energy bands. Valence band contains electrons from the lowest energy level to the energy level at the lower edge of the bandgap (Figure 7.45). Since filling of energy is from the lowest energy level, this band is usually almost full.

7.4.2.3.1.4 Conduction band

The conduction band consists of energy levels from the upper edge of the bandgap and higher (Figure 7.45). To reach the conduction band, the electrons in the valence band should have enough energy to cross the band gap. Once the electrons are excited, they subsequently relax back to the valence band (either radiatively or non-radiatively) followed by a subsequent emission of radiation. This property is responsible for most of the applications of quantum dots.

7.4.2.3.1.5 Exciton and exciton Bohr radius

When an electron is excited from the valence band to the conduction band, corresponding to the electron in the conduction band a hole (absence of electron) is formed in the valence band. This electron pair is called an exciton. Excitons have a natural separation distance between the electron and hole, which is characteristic of the material. This average distance is called exciton Bohr radius. In a bulk semiconductor, the size of the crystal is much larger than the exciton Bohr radius and hence the exciton is free to move throughout the crystal.

7.4.2.3.2 Energy levels in a quantum dot semiconductor

Before understanding the electronic structure of a quantum dot semiconductor, it is important to understand what a quantum dot nanoparticle is. We earlier studied that a nanoparticle is any particle with one of its dimensions in the 1 - 100 nm. A quantum dot is a nanoparticle with its diameter on the order of the materials exciton Bohr radius. Quantum dots are typically 2 - 10 nm wide and approximately consist of 10 to 50 atoms. With this understanding of a quantum dot semiconductor, the electronic structure of a quantum dot semiconductor can be described by the following terms.

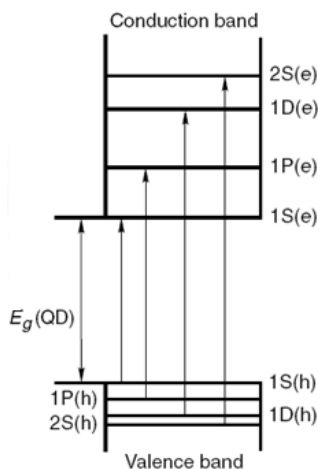


Figure 7.46: Energy levels in quantum dot. Allowed optical transitions are shown. Adapted from T. Pradeep, *Nano: The Essentials. Understanding Nanoscience and Nanotechnology*, Tata McGraw-Hill, New Delhi (2007).

7.4.2.3.2.1 Quantum confinement

When the size of the semiconductor crystal becomes comparable or smaller than the exciton Bohr radius, the quantum dots are in a state of quantum confinement. As a result of quantum confinement, the energy levels in a quantum dot are discrete (Figure 7.46) as opposed to being continuous in a bulk crystal (Figure 7.45).

7.4.2.3.2.2 Discrete energy levels

In materials that have small number of atoms and are considered as quantum confined, the energy levels are separated by an appreciable amount of energy such that they are not continuous, but are discrete (see Figure 7.46). The energy associated with an electron (equivalent to conduction band energy level) is given by is given by (7.13), where h is the Planck's constant, m_e is the effective mass of electron and n is the quantum number for the conduction band states, and n can take the values 1, 2, 3 and so on. Similarly, the energy associated with the hole (equivalent to valence band energy level) is given by (7.14), where n' is the quantum number for the valence states, and n' can take the values 1, 2, 3, and so on. The energy increases as one goes higher in the quantum number. Since the electron mass is much smaller than that of the hole, the electron levels are separated more widely than the hole levels.

$$E^e = \frac{h^2 n^2}{8\pi^2 m_e d^2} \quad (7.13)$$

$$E^h = \frac{h^2 n'^2}{8\pi^2 m_h d^2} \quad (7.14)$$

7.4.2.3.2.3 Tunable band gap

As seen from (7.13) and (7.14), the energy levels are affected by the diameter of the semiconductor particles. If the diameter is very small, since the energy is dependent on inverse of diameter squared, the energy levels of the upper edge of the band gap (lowest conduction band level) and lower edge of the band gap (highest valence band level) change significantly with the diameter of the particle and the effective mass of the electron and the hole, resulting in a size dependent tunable band gap. This also results in the discretization of the energy levels.

Qualitatively, this can be understood in the following way. In a bulk semiconductor, the addition or removal of an atom is insignificant compared to the size of the bulk semiconductor, which consists of a large number of atoms. The large size of bulk semiconductors makes the changes in band gap so negligible on the addition of an atom, that it is considered as a fixed band gap. In a quantum dot, addition of an atom does make a difference, resulting in the tunability of band gap.

7.4.2.3.3 UV-visible absorbance

Due to the presence of discrete energy levels in a QD, there is a widening of the energy gap between the highest occupied electronic states and the lowest unoccupied states as compared to the bulk material. As a consequence, the optical properties of the semiconductor nanoparticles also become size dependent.

The minimum energy required to create an exciton is the defined by the band gap of the material, i.e., the energy required to excite an electron from the highest level of valence energy states to the lowest level of the conduction energy states. For a quantum dot, the bandgap varies with the size of the particle. From (7.13) and (7.14), it can be inferred that the band gap becomes higher as the particle becomes smaller. This means that for a smaller particle, the energy required for an electron to get excited is higher. The relation between energy and wavelength is given by (7.15), where h is the Planck's constant, c is the speed of light, λ

is the wavelength of light. Therefore, from (7.15) to cross a bandgap of greater energy, shorter wavelengths of light are absorbed, i.e., a blue shift is seen.

$$E = \frac{hc}{\lambda} \quad (7.15)$$

For Group 12-16 semiconductors, the bandgap energy falls in the UV-visible range. That is ultraviolet light or visible light can be used to excite an electron from the ground valence states to the excited conduction states. In a bulk semiconductor the band gap is fixed, and the energy states are continuous. This results in a rather uniform absorption spectrum (Figure 7.47a).

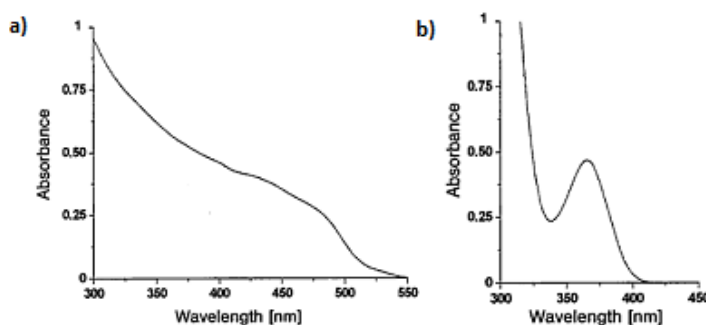


Figure 7.47: UV-vis spectra of (a) bulk CdS and (b) 4 nm CdS. Adapted from G. Kickelbick, *Hybrid Materials: Synthesis, Characterization and Applications*, Wiley-VCH, Weinheim (2007).

In the case of Group 12-16 quantum dots, since the bandgap can be changed with the size, these materials can absorb over a range of wavelengths. The peaks seen in the absorption spectrum (Figure 7.47b) correspond to the optical transitions between the electron and hole levels. The minimum energy and thus the maximum wavelength peak corresponds to the first exciton peak or the energy for an electron to get excited from the highest valence state to the lowest conduction state. The quantum dot will not absorb wavelengths of energy longer than this wavelength. This is known as the absorption onset.

7.4.2.3.4 Fluorescence

Fluorescence is the emission of electromagnetic radiation in the form of light by a material that has absorbed a photon. When a semiconductor quantum dot (QD) absorbs a photon/energy equal to or greater than its band gap, the electrons in the QD's get excited to the conduction state. This excited state is however not stable. The electron can relax back to its ground state by either emitting a photon or lose energy via heat losses. These processes can be divided into two categories – radiative decay and non-radiative decay. Radiative decay is the loss of energy through the emission of a photon or radiation. Non-radiative decay involves the loss of heat through lattice vibrations and this usually occurs when the energy difference between the levels is small. Non-radiative decay occurs much faster than radiative decay.

Usually the electron relaxes to the ground state through a combination of both radiative and non-radiative decays. The electron moves quickly through the conduction energy levels through small non-radiative decays and the final transition across the band gap is via a radiative decay. Large nonradiative decays don't occur across the band gap because the crystal structure can't withstand large vibrations without breaking the bonds of the crystal. Since some of the energy is lost through the non-radiative decay, the energy of the emitted photon, through the radiative decay, is much lesser than the absorbed energy. As a result the

wavelength of the emitted photon or fluorescence is longer than the wavelength of absorbed light. This energy difference is called the Stokes shift. Due this Stokes shift, the emission peak corresponding to the absorption band edge peak is shifted towards a higher wavelength (lower energy), i.e., Figure 7.48.

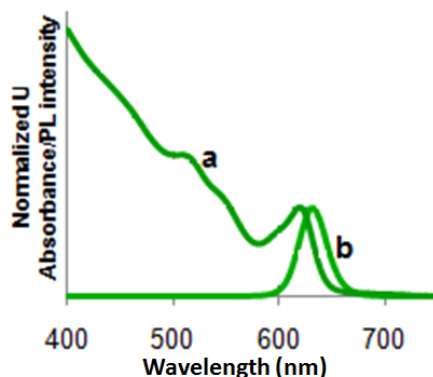


Figure 7.48: Absorption spectra (a) and emission spectra (b) of CdSe tetrapod.

Intensity of emission versus wavelength is a bell-shaped Gaussian curve. As long as the excitation wavelength is shorter than the absorption onset, the maximum emission wavelength is independent of the excitation wavelength. Figure 7.48 shows a combined absorption and emission spectrum for a typical CdSe tetrapod.

7.4.2.3.5 Factors affecting the optical properties of NPs

There are various factors that affect the absorption and emission spectra for Group 12-16 semiconductor quantum crystals. Fluorescence is much more sensitive to the background, environment, presence of traps and the surface of the QDs than UV-visible absorption. Some of the major factors influencing the optical properties of quantum nanoparticles include:

- **Surface defects, imperfection of lattice, surface charges** – The surface defects and imperfections in the lattice structure of semiconductor quantum dots occur in the form of unsatisfied valencies. Similar to surface charges, unsatisfied valencies provide a sink for the charge carriers, resulting in unwanted recombinations.
- **Surface ligands** – The presence of surface ligands is another factor that affects the optical properties. If the surface ligand coverage is a 100%, there is a smaller chance of surface recombinations to occur.
- **Solvent polarity** – The polarity of solvents is very important for the optical properties of the nanoparticles. If the quantum dots are prepared in organic solvent and have an organic surface ligand, the more non-polar the solvent, the particles are more dispersed. This reduces the loss of electrons through recombinations again, since when particles come in close proximity to each other, increases the non-radiative decay events.

7.4.2.3.6 Applications of the optical properties of Group 12-16 semiconductor NPs

The size dependent optical properties of NP's have many applications from biomedical applications to solar cell technology, from photocatalysis to chemical sensing. Most of these applications use the following unique properties.

For applications in the field of nanoelectronics, the sizes of the quantum dots can be tuned to be comparable to the scattering lengths, reducing the scattering rate and hence, the signal to noise ratio. For Group 12-16 QDs to be used in the field of solar cells, the bandgap of the particles can be tuned so as to form absorb energy over a large range of the solar spectrum, resulting in more number of excitons and hence more electricity. Since the nanoparticles are so small, most of the atoms are on the surface. Thus, the surface to volume ratio is very large for the quantum dots. In addition to a high surface to volume ratio, the Group 12-16 QDs respond to light energy. Thus quantum dots have very good photocatalytic properties. Quantum dots show fluorescence properties, and emit visible light when excited. This property can be used for applications as biomarkers. These quantum dots can be tagged to drugs to monitor the path of the drugs. Specially shaped Group 12-16 nanoparticles such as hollow shells can be used as drug delivery agents. Another use for the fluorescence properties of Group 12-16 semiconductor QDs is in color-changing paints, which can change colors according to the light source used.

7.4.2.3.7 Bibliography

- M. J. Schulz, V. N. Shanov, and Y. Yun, *Nanomedicine - Design of Particles, Sensors, Motors, Implants, Robots, and Devices*, Artech House, London (2009).
- S. V. Gapoenko, *Optical Properties of Semiconductor Nanocrystals*, Cambridge University Press, Cambridge (2003).
- T. Pradeep, *Nano: The Essentials. Understanding Nanoscience and Nanotechnology*, Tata McGraw-Hill, New Delhi (2007).
- G. Schmid, *Nanoparticles: From Theory to Application*, Wiley-VCH, Weinheim (2004).
- A. L. Rogach, *Semiconductor Nanocrystal Quantum Dots. Synthesis, Assembly, Spectroscopy and Applications*, Springer Wien, New York (2008).
- G. Kickelbick, *Hybrid Materials: Synthesis, Characterization and Applications*, Wiley-VCH, Weinheim (2007).

7.4.3 Characterization of Group 12-16 (II-VI) Semiconductor Nanoparticles by UV-visible Spectroscopy¹⁰

Quantum dots (QDs) as a general term refer to nanocrystals of semiconductor materials, in which the size of the particles are comparable to the natural characteristic separation of an electron-hole pair, otherwise known as the exciton Bohr radius of the material. When the size of the semiconductor nanocrystal becomes this small, the electronic structure of the crystal is governed by the laws of quantum physics. Very small Group 12-16 (II-VI) semiconductor nanoparticle quantum dots, in the order of 2 - 10 nm, exhibit significantly different optical and electronic properties from their bulk counterparts. The characterization of size dependent optical properties of Group 12-16 semiconductor particles provide a lot of qualitative and quantitative information about them – size, quantum yield, monodispersity, shape and presence of surface defects. A combination of information from both the UV-visible absorption and fluorescence, complete the analysis of the optical properties.

7.4.3.1 UV-visible absorbance spectroscopy

Absorption spectroscopy, in general, refers to characterization techniques that measure the absorption of radiation by a material, as a function of the wavelength. Depending on the source of light used, absorption spectroscopy can be broadly divided into infrared and UV-visible spectroscopy. The band gap of Group 12-16 semiconductors is in the UV-visible region. This means the minimum energy required to excite an electron from the valence states of the Group 12-16 semiconductor QDs to its conduction states, lies in the UV-visible region. This is also a reason why most of the Group 12-16 semiconductor quantum dot solutions are colored.

¹⁰This content is available online at <<http://cnx.org/content/m34601/1.1/>>.

This technique is complementary to fluorescence spectroscopy, in that UV-visible spectroscopy measures electronic transitions from the ground state to the excited state, whereas fluorescence deals with the transitions from the excited state to the ground state. In order to characterize the optical properties of a quantum dot, it is important to characterize the sample with both these techniques

In quantum dots, due to the very small number of atoms, the addition or removal of one atom to the molecule changes the electronic structure of the quantum dot dramatically. Taking advantage of this property in Group 12-16 semiconductor quantum dots, it is possible to change the band gap of the material by just changing the size of the quantum dot. A quantum dot can absorb energy in the form of light over a range of wavelengths, to excite an electron from the ground state to its excited state. The minimum energy that is required to excite an electron, is dependent on the band gap of the quantum dot. Thus, by making accurate measurements of light absorption at different wavelengths in the ultraviolet and visible spectrum, a correlation can be made between the band gap and size of the quantum dot. Group 12-16 semiconductor quantum dots are of particular interest, since their band gap lies in the visible region of the solar spectrum.

The UV-visible absorbance spectroscopy is a characterization technique in which the absorbance of the material is studied as a function of wavelength. The visible region of the spectrum is in the wavelength range of 380 nm (violet) to 740 nm (red) and the near ultraviolet region extends to wavelengths of about 200 nm. The UV-visible spectrophotometer analyzes over the wavelength range 200 – 900 nm.

When the Group 12-16 semiconductor nanocrystals are exposed to light having an energy that matches a possible electronic transition as dictated by laws of quantum physics, the light is absorbed and an exciton pair is formed. The UV-visible spectrophotometer records the wavelength at which the absorption occurs along with the intensity of the absorption at each wavelength. This is recorded in a graph of absorbance of the nanocrystal versus wavelength.

7.4.3.2 Instrumentation

A working schematic of the UV-visible spectrophotometer is shown in Figure 7.49.

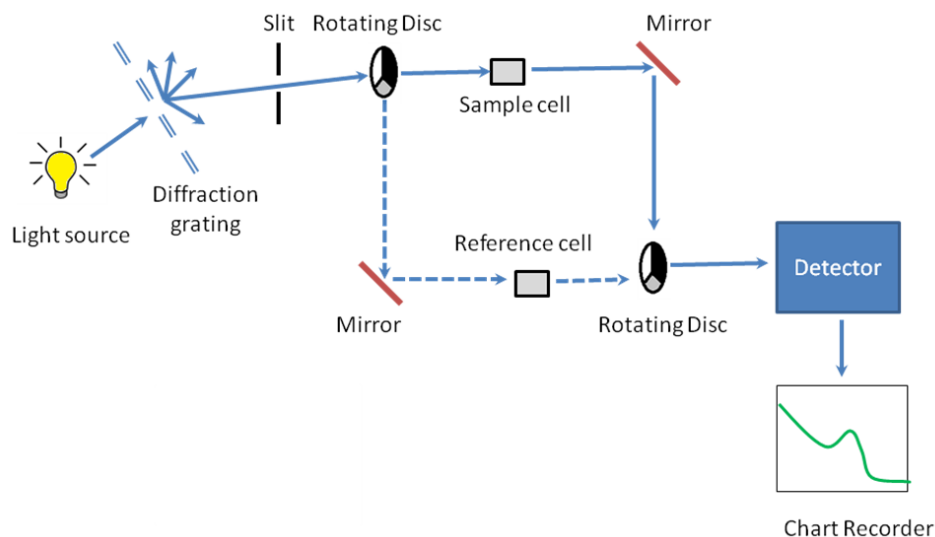


Figure 7.49: Schematic of UV-visible spectrophotometer.

7.4.3.2.1 The light source

Since it is a UV-vis spectrophotometer, the light source (Figure 7.49) needs to cover the entire visible and the near ultra-violet region (200 - 900 nm). Since it is not possible to get this range of wavelengths from a single lamp, a combination of a deuterium lamp for the UV region of the spectrum and tungsten or halogen lamp for the visible region is used. This output is then sent through a diffraction grating as shown in the schematic.

7.4.3.2.2 The diffraction grating and the slit

The beam of light from the visible and/or UV light source is then separated into its component wavelengths (like a very efficient prism) by a diffraction grating (Figure 7.49). Following the slit is a slit that sends a monochromatic beam into the next section of the spectrophotometer.

7.4.3.2.3 Rotating discs

Light from the slit then falls onto a rotating disc (Figure 7.49). Each disc consists of different segments – an opaque black section, a transparent section and a mirrored section. If the light hits the transparent section, it will go straight through the sample cell, get reflected by a mirror, hits the mirrored section of a second rotating disc, and then collected by the detector. Else if the light hits the mirrored section, gets reflected by a mirror, passes through the reference cell, hits the transparent section of a second rotating disc and then collected by the detector. Finally if the light hits the black opaque section, it is blocked and no light passes through the instrument, thus enabling the system to make corrections for any current generated by the detector in the absence of light.

7.4.3.2.4 Sample cell, reference cell and sample preparation

For liquid samples, a square cross section tube sealed at one end is used. The choice of cuvette depends on the following factors:

- **Type of solvent** - For aqueous samples, specially designed rectangular quartz, glass or plastic cuvettes are used. For organic samples glass and quartz cuvettes are used.
- **Excitation wavelength** – Depending on the size and thus, bandgap of the 12-16 semiconductor nanoparticles, different excitation wavelengths of light are used. Depending on the excitation wavelength, different materials are used

Cuvette	Wavelength (nm)
Visible only glass	380 - 780
Visible only plastic	380 - 780
UV plastic	220 - 780
Quartz	200 - 900

Table 7.3: Cuvette materials and their wavelengths.

- **Cost** – Plastic cuvettes are the least expensive and can be discarded after use. Though quartz cuvettes have the maximum utility, they are the most expensive, and need to be reused. Generally, disposable plastic cuvettes are used when speed is more important than high accuracy.

The best cuvettes need to be very clear and have no impurities that might affect the spectroscopic reading. Defects on the cuvette such as scratches, can scatter light and hence should be avoided. Some cuvettes are clear only on two sides, and can be used in the UV-Visible spectrophotometer, but cannot be used for

fluorescence spectroscopy measurements. For Group 12-16 semiconductor nanoparticles prepared in organic solvents, the quartz cuvette is chosen.

In the sample cell the quantum dots are dispersed in a solvent, whereas in the reference cell the pure solvent is taken. It is important that the sample be very dilute (maximum first exciton absorbance should not exceed 1 au) and the solvent is not UV-visible active. For these measurements, it is required that the solvent does not have characteristic absorption or emission in the region of interest. Solution phase experiments are preferred, though it is possible to measure the spectra in the solid state also using thin films, powders, etc. The instrumentation for solid state UV-visible absorption spectroscopy is slightly different from the solution phase experiments and is beyond the scope of discussion.

7.4.3.2.5 Detector

Detector converts the light into a current signal that is read by a computer. Higher the current signal, greater is the intensity of the light. The computer then calculates the absorbance using the in (7.16), where A denotes absorbance, I is sample cell intensity and I_0 is the reference cell intensity.

$$A = \log_{10}(I_0/I) \quad (7.16)$$

The following cases are possible:

- Where $I < I_0$ and $A < 0$. This usually occurs when the solvent absorbs in the wavelength range. Preferably the solvent should be changed, to get an accurate reading for actual reference cell intensity.
- Where $I = I_0$ and $A = 0$. This occurs when pure solvent is put in both reference and sample cells. This test should always be done before testing the sample, to check for the cleanliness of the cuvettes.
- When $A = 1$. This occurs when 90% of the light at a particular wavelength has been absorbed, which means that only 10% is seen at the detector. So I_0/I becomes $100/10 = 10$. $\log_{10}$ of 10 is 1.
- When $A > 1$. This occurs in extreme case where more than 90% of the light is absorbed.

7.4.3.2.6 Output

The output is the form of a plot of absorbance against wavelength, e.g., Figure 7.50.

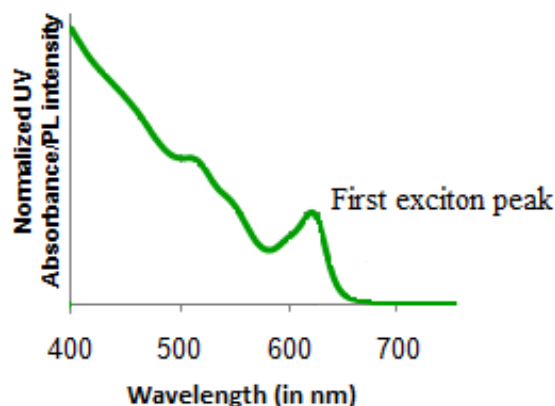


Figure 7.50: Representative UV-visible absorption spectrum for CdSe tetrapods.

7.4.3.3 Beer-Lambert law

In order to make comparisons between different samples, it is important that all the factors affecting absorbance should be constant except the sample itself.

7.4.3.3.1 Effect of concentration on absorbance

The extent of absorption depends on the number of absorbing nanoparticles or in other words the concentration of the sample. If it is a reasonably concentrated solution, it will have a high absorbance since there are lots of nanoparticles to interact with the light. Similarly in an extremely dilute solution, the absorbance is very low. In order to compare two solutions, it is important that we should make some allowance for the concentration.

7.4.3.3.2 Effect of container shape

Even if we had the same concentration of solutions, if we compare two solutions – one in a rectangular shaped container (e.g., Figure 7.51) so that light travelled 1 cm through it and the other in which the light travelled 100 cm through it, the absorbance would be different. This is because if the length the light travelled is greater, it means that the light interacted with more number of nanocrystals, and thus has a higher absorbance. Again, in order to compare two solutions, it is important that we should make some allowance for the concentration.



Figure 7.51: A typical rectangular cuvette for UV-visible spectroscopy.

7.4.3.3.3 The law

The Beer-Lambert law addresses the effect of concentration and container shape as shown in (7.16), (7.17) and (7.18), where A denotes absorbance; ϵ is the molar absorptivity or molar absorption coefficient; l is the path length of light (in cm); and c is the concentration of the solution (mol/dm^3).

$$\log_{10}(I_0/I) = \epsilon lc \quad (7.17)$$

$$A = \epsilon lc \quad (7.18)$$

7.4.3.3.4 Molar absorptivity

From the Beer-Lambert law, the molar absorptivity ' ε ' can be expressed as shown in (7.19).

$$c = A/\ell\varepsilon \quad (7.19)$$

Molar absorptivity corrects for the variation in concentration and length of the solution that the light passes through. It is the value of absorbance when light passes through 1 cm of a 1 mol/dm³ solution.

7.4.3.3.5 Limitations of Beer-Lambert law

The linearity of the Beer-Lambert law is limited by chemical and instrumental factors.

- At high concentrations (> 0.01 M), the relation between absorptivity coefficient and absorbance is no longer linear. This is due to the electrostatic interactions between the quantum dots in close proximity.
- If the concentration of the solution is high, another effect that is seen is the scattering of light from the large number of quantum dots.
- The spectrophotometer performs calculations assuming that the refractive index of the solvent does not change significantly with the presence of the quantum dots. This assumption only works at low concentrations of the analyte (quantum dots).
- Presence of stray light.

7.4.3.4 Analysis of data

The data obtained from the spectrophotometer is a plot of absorbance as a function of wavelength. Quantitative and qualitative data can be obtained by analysing this information

7.4.3.4.1 Quantitative Information

The band gap of the semiconductor quantum dots can be tuned with the size of the particles. The minimum energy for an electron to get excited from the ground state is the energy to cross the band gap. In an absorption spectra, this is given by the first exciton peak at the maximum wavelength ($\lambda_{\max}$).

7.4.3.4.1.1 Size of the quantum dots

The size of quantum dots can be approximated corresponding to the first exciton peak wavelength. Empirical relationships have been determined relating the diameter of the quantum dot to the wavelength of the first exciton peak. The Group 12-16 semiconductor quantum dots that they studied were cadmium selenide (CdSe), cadmium telluride (CdTe) and cadmium sulfide (CdS). The empirical relationships are determined by fitting experimental data of absorbance versus wavelength of known sizes of particles. The empirical equations determined are given for CdTe, CdSe, and CdS in (7.20), (7.21) and (7.22) respectively, where D is the diameter and λ is the wavelength corresponding to the first exciton peak. For example, if the first exciton peak of a CdSe quantum dot is 500 nm, the corresponding diameter of the quantum dot is 2.345 nm and for a wavelength of 609 nm, the corresponding diameter is 5.008 nm.

$$D = (9.8127 \times 10^{-7})\lambda^3 - (1.7147 \times 10^{-3})\lambda^2 + (1.0064)\lambda - 194.84 \quad (7.20)$$

$$D = (1.6122 \times 10^{-7})\lambda^3 - (2.6575 \times 10^{-6})\lambda^2 + (1.6242 \times 10^{-3})\lambda + 41.57 \quad (7.21)$$

$$D = (-6.6521 \times 10^{-8})\lambda^3 + (1.9577 \times 10^{-4})\lambda^2 - (9.2352 \times 10^{-2})\lambda + 13.29 \quad (7.22)$$

7.4.3.4.1.2 Concentration of sample

Using the Beer-Lambert law, it is possible to calculate the concentration of the sample if the molar absorptivity for the sample is known. The molar absorptivity can be calculated by recording the absorbance of a standard solution of 1 mol/dm^3 concentration in a standard cuvette where the light travels a constant distance of 1 cm. Once the molar absorptivity and the absorbance of the sample are known, with the length the light travels being fixed, it is possible to determine the concentration of the sample solution.

Empirical equations can be determined by fitting experimental data of extinction coefficient per mole of Group 12-16 semiconductor quantum dots, at 250°C , to the diameter of the quantum dot, (7.23), (7.24), and (7.25).

$$\varepsilon = 10043 \times D^{2.12} \quad (7.23)$$

$$\varepsilon = 5857 \times D^{2.65} \quad (7.24)$$

$$\varepsilon = 21536 \times D^{2.3} \quad (7.25)$$

The concentration of the quantum dots can then be determined by using the Beer Lambert law as given by (7.19).

7.4.3.4.2 Qualitative Information

Apart from quantitative data such as the size of the quantum dots and concentration of the quantum dots, a lot of qualitative information can be derived from the absorption spectra.

7.4.3.4.2.1 Size distribution

If there is a very narrow size distribution, the first exciton peak will be very sharp (Figure 7.52). This is because due to the narrow size distribution, the differences in band gap between different sized particles will be very small and hence most of the electrons will get excited over a smaller range of wavelengths. In addition, if there is a narrow size distribution, the higher exciton peaks are also seen clearly.

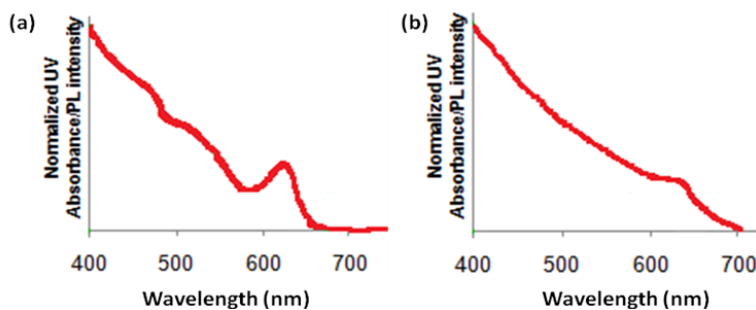


Figure 7.52: Narrow emission spectra (a) and broad emission spectra (b) of CdSe QDs.

7.4.3.4.2.2 Shaped particles

In the case of a spherical quantum dot, in all dimensions, the particle is quantum confined (Figure 7.53). In the case of a nanorod, whose length is not in the quantum regime, the quantum effects are determined by the width of the nanorod. Similar is the case in tetrapods or four legged structures. The quantum effects are determined by the thickness of the arms. During the synthesis of the shaped particles, the thickness of the rod or the arm of the tetrapod does not vary among the different particles, as much as the length of the rods or arms changes. Since the thickness of the rod or tetrapod is responsible for the quantum effects, the absorption spectrum of rods and tetrapods has sharper features as compared to a quantum dot. Hence, qualitatively it is possible to differentiate between quantum dots and other shaped particles.

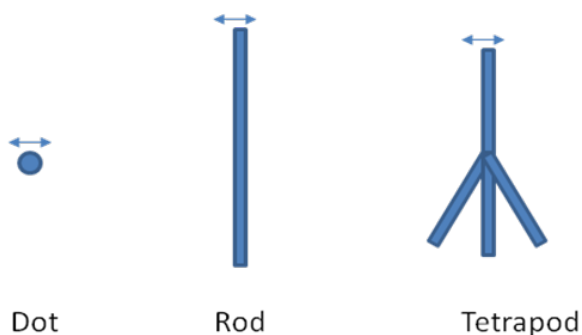


Figure 7.53: Different shaped nanoparticles with the arrows indicating the dimension where quantum confinement effects are observed.

7.4.3.4.2.3 Crystal lattice information

In the case of CdSe semiconductor quantum dots it has been shown that it is possible to estimate the crystal lattice of the quantum dot from the adsorption spectrum (Figure 7.54), and hence determine if the structure is zinc blend or wurtzite.

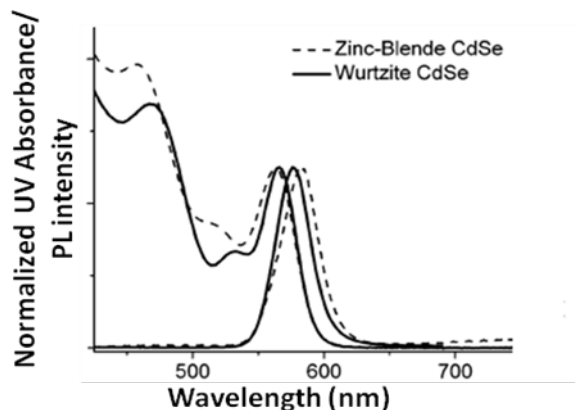


Figure 7.54: Zinc blende and wurtzite CdSe absorption spectra. Adapted from J. Jasieniak, C. Bullen, J. van Embden, and P. Mulvaney, *J. Phys. Chem. B*, 2005, **109**, 20665.

7.4.3.5 UV-vis absorption spectra of Group 12-16 semiconductor nanoparticles

7.4.3.5.1 Cadmium selenide

Cadmium selenide (CdSe) is one of the most popular Group 12-16 semiconductors. This is mainly because the band gap (712 nm or 1.74 eV) energy of CdSe. Thus, the nanoparticles of CdSe can be engineered to have a range of band gaps throughout the visible range, corresponding to the major part of the energy that comes from the solar spectrum. This property of CdSe along with its fluorescing properties is used in a variety of applications such as solar cells and light emitting diodes. Though cadmium and selenium are known carcinogens, the harmful biological effects of CdSe can be overcome by coating the CdSe with a layer of zinc sulfide. Thus CdSe, can also be used as bio-markers, drug-delivery agents, paints and other applications.

A typical absorption spectrum of narrow size distribution wurtzite CdSe quantum dot is shown in Figure 7.55. A size evolving absorption spectra is shown in Figure 7.56. However, a complete analysis of the sample is possible only by also studying the fluorescence properties of CdSe.

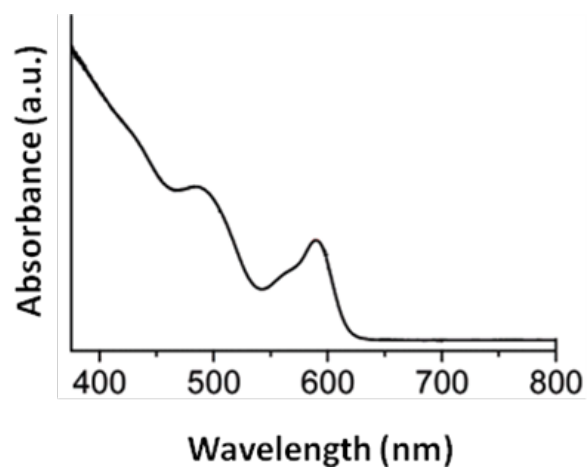


Figure 7.55: Wurtzite CdSe quantum dot. Adapted from X. Zhong, Y. Feng, and Y. Zhang, *J. Phys. Chem. C*, 2007, **111**, 526.

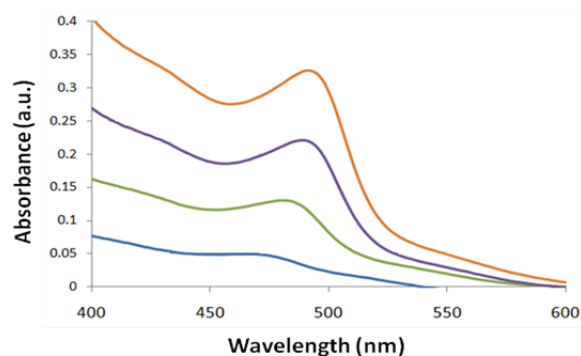


Figure 7.56: Size evolving absorption spectra of CdSe quantum dots.

7.4.3.5.2 Cadmium telluride (CdTe)

Cadmium telluride has a band gap of 1.44 eV (860 nm) and as such it absorbs in the infrared region. Like CdSe, the sizes of CdTe can be engineered to have different band edges and thus, different absorption spectra as a function of wavelength. A typical CdTe spectra is shown in Figure 7.57. Due to the small bandgap energy of CdTe, it can be used in tandem with CdSe to absorb in a greater part of the solar spectrum.

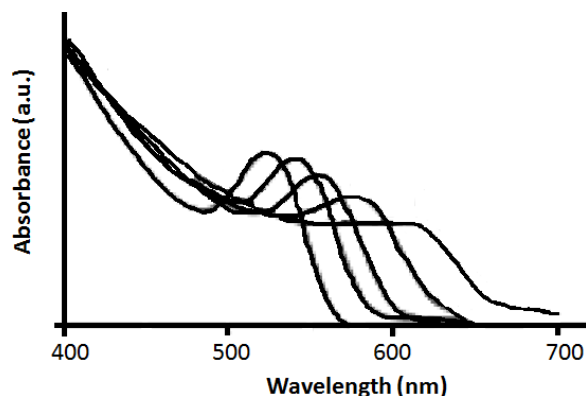


Figure 7.57: Size evolving absorption spectra of CdTe quantum dots from 3 nm to 7 nm. Adapted from C. Qi-Fan, W. Wen-Xing, G. Ying-Xin, L. Meng-Ying, X. Shu-Kun and Z. Xiu-Juan, *Chin. J. Anal. Chem.*, 2007, **35**, 135.

7.4.3.5.3 Other Group 12-16 semiconductor systems

Table 7.4 shows the bulk band gap of other Group 12-16 semiconductor systems. The band gap of ZnS falls in the UV region, while those of ZnSe, CdS, and ZnTe fall in the visible region.

Material	Band gap (eV)	Wavelength (nm)
ZnS	3.61	343.2
ZnSe	2.69	460.5
ZnTe	2.39	518.4
CdS	2.49	497.5
CdSe	1.74	712.1
CdTe	1.44	860.3

Table 7.4: Bulk band gaps of different Group 12-16 semiconductors.

7.4.3.5.4 Heterostructures of Group 12-16 semiconductor systems

It is often desirable to have a combination of two Group 12-16 semiconductor system quantum heterostructures of different shapes like dots and tetrapods, for applications in solar cells, bio-markers, etc. Some of the most interesting systems are ZnS shell-CdSe core systems, such as the CdSe/CdS rods and tetrapods.

Figure 7.58 shows a typical absorption spectra of CdSe-ZnS core-shell system. This system is important because of the drastically improved fluorescence properties because of the addition of a wide band gap ZnS shell than the core CdSe. In addition with a ZnS shell, CdSe becomes bio-compatible.

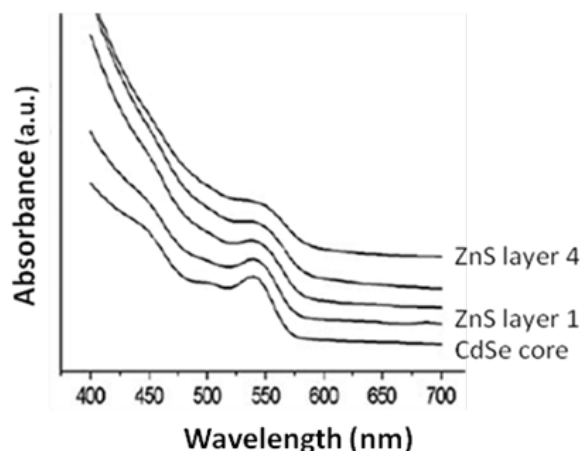


Figure 7.58: Absorption spectra of CdSe core, ZnS shell. Adapted from C. Qing-Zhu, P. Wang, X. Wang and Y. Li, *Nanoscale Res. Lett.*, 2008, **3**, 213.

A CdSe seed, CdS arm nanorods system is also interesting. Combining CdSe and CdS in a single nanostructure creates a material with a mixed dimensionality where holes are confined to CdSe while electrons can move freely between CdSe and CdS phases.

7.4.3.6 Bibliography

- S. V. Gapoenko, *Optical Properties of Semiconductor Nanocrystals*, Cambridge University Press, Cambridge (2003).
- W. W. Yu, L. Qu, W. Guo, and X. Peng, *Chem. Mater.*, 2003, **15**, 2854.
- J. Jasieniak, C. Bullen, J. van Embden, and P. Mulvaney, *J. Phys. Chem. B*, 2005, **109**, 20665.
- X. Zhong, Y. Feng, and Y. Zhang, *J. Phys. Chem. C*, 2007, **111**, 526.
- D. V. Talapin, J. H. Nelson, E. V. Shevchenko, S. Aloni, B. Sadtler, and A. P. Alivisatos, *Nano Lett.*, 2007, **7**, 2951.
- C. Qing-Zhu, P. Wang, X. Wang, and Y. Li, *Nanoscale Res. Lett.*, 2008, **3**, 213.
- C. Qi-Fan, W. Wen-Xing, G. Ying-Xin, L. Meng-Ying, X. Shu-Kun, and Z. Xiu-Juan, *Chin. J. Anal. Chem.*, 2007, **35**, 135.

7.4.4 Optical Characterization of Group 12-16 (II-VI) Semiconductor Nanoparticles by Fluorescence Spectroscopy¹¹

Group 12-16 semiconductor nanocrystals when exposed to light of a particular energy absorb light to excite electrons from the ground state to the excited state, resulting in the formation of an electron-hole pair (also known as excitons). The excited electrons relax back to the ground state, mainly through radiative emission of energy in the form of photons.

Quantum dots (QD) refer to nanocrystals of semiconductor materials where the size of the particles is comparable to the natural characteristic separation of an electron-hole pair, otherwise known as the exciton Bohr radius of the material. In quantum dots, the phenomenon of emission of photons associated with the transition of electrons from the excited state to the ground state is called fluorescence.

¹¹This content is available online at <<http://cnx.org/content/m34656/1.1/>>.

7.4.4.1 Fluorescence spectroscopy

Emission spectroscopy, in general, refers to a characterization technique that measures the emission of radiation by a material that has been excited. Fluorescence spectroscopy is one type of emission spectroscopy which records the intensity of light radiated from the material as a function of wavelength. It is a non-destructive characterization technique.

After an electron is excited from the ground state, it needs to relax back to the ground state. This relaxation or loss of energy to return to the ground state, can be achieved by a combination of non-radiative decay (loss of energy through heat) and radiative decay (loss of energy through light). Non-radiative decay by vibrational modes typically occurs between energy levels that are close to each other. Radiative decay by the emission of light occurs when the energy levels are far apart like in the case of the band gap. This is because loss of energy through vibrational modes across the band gap can result in breaking the bonds of the crystal. This phenomenon is shown in Figure 7.59.

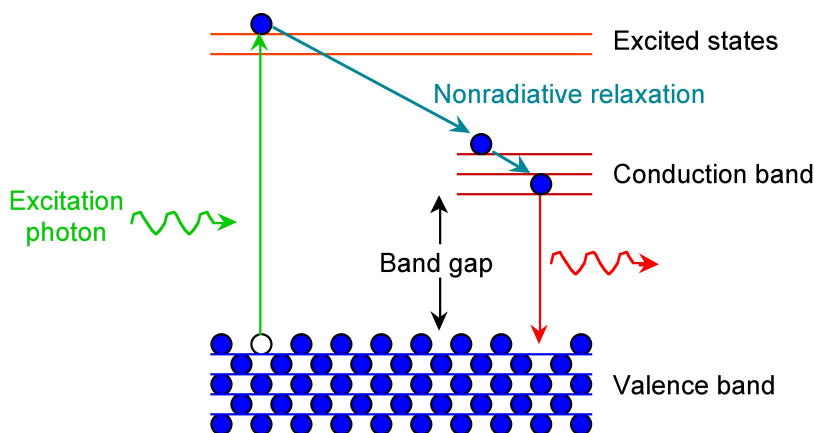


Figure 7.59: Emission of luminescence photon for Group 12-16 semiconductor quantum dot.

The band gap of Group 12-16 semiconductors is in the UV-visible region. Thus, the wavelength of the emitted light as a result of radiative decay is also in the visible region, resulting in fascinating fluorescence properties.

A fluorimeter is a device that records the fluorescence intensity as a function of wavelength. The fluorescence quantum yield can then be calculated by the ratio of photons absorbed to photons emitted by the system. The quantum yield gives the probability of the excited state getting relaxed via fluorescence rather than by any other non-radiative decay.

7.4.4.2 Difference between fluorescence and phosphorescence

Photoluminescence is the emission of light from any material due to the loss of energy from excited state to ground state. There are two main types of luminescence – fluorescence and phosphorescence. Fluorescence is a fast decay process, where the emission rate is around 10^8 s^{-1} and the lifetime is around $10^{-9} - 10^{-7} \text{ s}$. Fluorescence occurs when the excited state electron has an opposite spin compared to the ground state electrons. From the laws of quantum mechanics, this is an allowed transition, and occurs rapidly by emission of a photon. Fluorescence disappears as soon as the exciting light source is removed.

Phosphorescence is the emission of light, in which the excited state electron has the same spin orientation as the ground state electron. This transition is a forbidden one and hence the emission rates are slow ($10^3 -$

10^0 s^{-1}). So the phosphorescence lifetimes are longer, typically seconds to several minutes, while the excited phosphors slowly returned to the ground state. Phosphorescence is still seen, even after the exciting light source is removed. Group 12-16 semiconductor quantum dots exhibit fluorescence properties when excited with ultraviolet light.

7.4.4.3 Instrumentation

The working schematic for the fluorometer is shown in Figure 7.60.

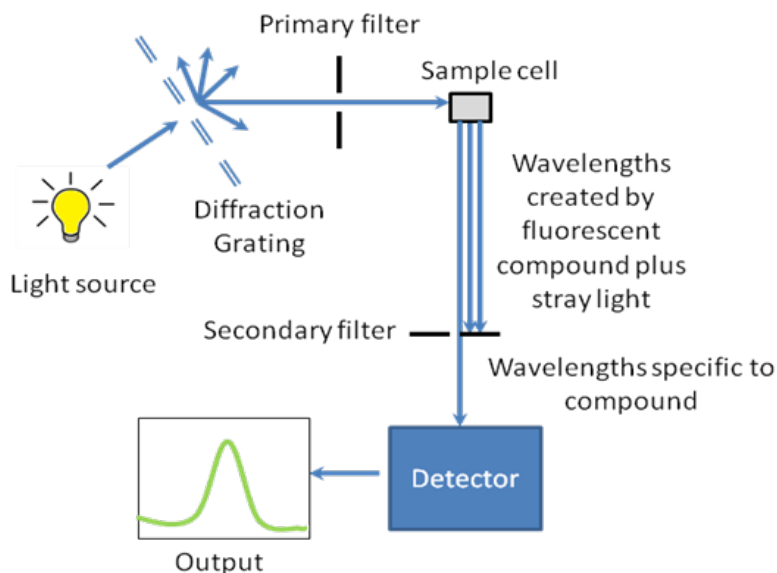


Figure 7.60: Schematic of fluorometer.

7.4.4.3.1 The light source

The excitation energy is provided by a light source that can emit wavelengths of light over the ultraviolet and the visible range. Different light sources can be used as excitation sources such as lasers, xenon arcs and mercury-vapor lamps. The choice of the light source depends on the sample. A laser source emits light of a high irradiance at a very narrow wavelength interval. This makes the need for the filter unnecessary, but the wavelength of the laser cannot be altered significantly. The mercury vapor lamp is a discrete line source. The xenon arc has a continuous emission spectrum between the ranges of 300 - 800 nm.

7.4.4.3.2 The diffraction grating and primary filter

The diffraction grating splits the incoming light source into its component wavelengths (Figure 7.60). The monochromator can then be adjusted to choose with wavelengths to pass through. Following the primary filter, specific wavelengths of light are irradiated onto the sample

7.4.4.3.3 Sample cell and sample preparation

A proportion of the light from the primary filter is absorbed by the sample. After the sample gets excited, the fluorescent substance returns to the ground state, by emitting a longer wavelength of light in all directions (Figure 7.60). Some of this light passes through a secondary filter. For liquid samples, a square cross section tube sealed at one end and all four sides clear, is used as a sample cell. The choice of cuvette depends on three factors:

1. **Type of solvent** - For aqueous samples, specially designed rectangular quartz, glass or plastic cuvettes are used. For organic samples glass and quartz cuvettes are used.
2. **Excitation wavelength** – Depending on the size and thus, bandgap of the Group 12-16 semiconductor nanoparticles, different excitation wavelengths of light are used. Depending on the excitation wavelength, different materials are used (Table 7.5).

Cuvette	Wavelength (nm)
Visible only glass	380 - 780
Visible only plastic	380 - 780
UV plastic	220 - 780
Quartz	200 - 900

Table 7.5: Cuvette materials and their wavelengths.

3. **Cost** – Plastic cuvettes are the least expensive and can be discarded after use. Though quartz cuvettes have the maximum utility, they are the most expensive, and need to be reused. Generally, disposable plastic cuvettes are used when speed is more important than high accuracy.



Figure 7.61: A typical cuvette for fluorescence spectroscopy.

The cuvettes have a 1 cm path length for the light (Figure 7.61). The best cuvettes need to be very clear and have no impurities that might affect the spectroscopic reading. Defects on the cuvette, such as scratches, can scatter light and hence should be avoided. Since the specifications of a cuvette are the same for both, the UV-visible spectrophotometer and fluorimeter, the same cuvette that is used to measure absorbance can be used to measure the fluorescence. For Group 12-16 semiconductor nanoparticles prepared in organic solvents, the clear four sided quartz cuvette is used. The sample solution should be dilute (absorbance <1 au), to avoid very high signal from the sample to burn out the detector. The solvent used to disperse the nanoparticles should not absorb at the excitation wavelength.

7.4.4.3.4 Secondary filter

The secondary filter is placed at a 90° angle (Figure 7.60) to the original light path to minimize the risk of transmitted or reflected incident light reaching the detector. Also this minimizes the amount of stray light, and results in a better signal-to-noise ratio. From the secondary filter, wavelengths specific to the sample are passed onto the detector.

7.4.4.3.5 Detector

The detector can either be single-channeled or multichanneled (Figure 7.60). The single-channeled detector can only detect the intensity of one wavelength at a time, while the multichanneled detects the intensity at all wavelengths simultaneously, making the emission monochromator or filter unnecessary. The different types of detectors have both advantages and disadvantages.

7.4.4.3.6 Output

The output is the form of a plot of intensity of emitted light as a function of wavelength as shown in Figure 7.62.

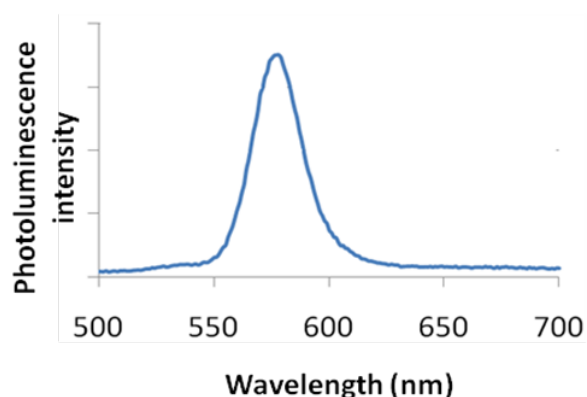


Figure 7.62: Emission spectra of CdSe quantum dot.

7.4.4.4 Analysis of data

The data obtained from fluorimeter is a plot of fluorescence intensity as a function of wavelength. Quantitative and qualitative data can be obtained by analysing this information.

7.4.4.4.1 Quantitative information

From the fluorescence intensity versus wavelength data, the quantum yield (Φ_F) of the sample can be determined. Quantum yield is a measure of the ratio of the photons absorbed with respect to the photons emitted. It is important for the application of Group 12-16 semiconductor quantum dots using their fluorescence properties, for e.g., bio-markers.

The most well-known method for recording quantum yield is the comparative method which involves the use of well characterized standard solutions. If a test sample and a standard sample have similar absorbance values at the same excitation wavelength, it can be assumed that the number of photons being absorbed by

both the samples is the same. This means that a ratio of the integrated fluorescence intensities of the test and standard sample measured at the same excitation wavelength will give a ratio of quantum yields. Since the quantum yield of the standard solution is known, the quantum yield for the unknown sample can be calculated.

A plot of integrated fluorescence intensity versus absorbance at the excitation wavelength is shown in Figure 7.63. The slope of the graphs shown in Figure 7.63 are proportional to the quantum yield of the different samples. Quantum yield is then calculated using (7.26), where subscripts ST denotes standard sample and X denotes the test sample; QY is the quantum yield; RI is the refractive index of the solvent.

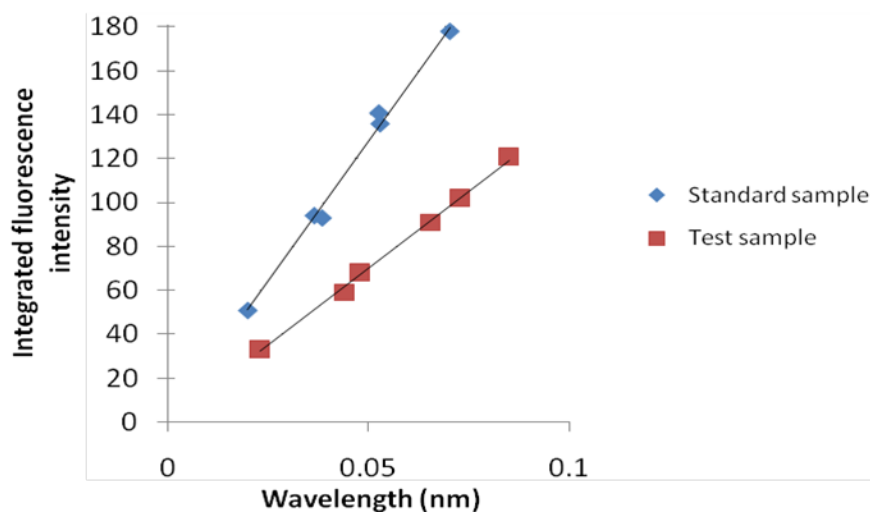


Figure 7.63: Integrated fluoresncene intensity as a function of absorbance.

$$\frac{QY_X}{QY_{ST}} = \frac{\text{slope}_X (RI_X)^2}{\text{slope}_{ST} (RI_{ST})^2} \quad (7.26)$$

Take the example of Figure 7.63. If the same solvent is used in both the sample and the standard solution, the ratio of quantum yields of the sample to the standard is given by (7.27). If the quantum yield of the standard is known to 0.95, then the quantum yield of the test sample is 0.523 or 52.3%.

$$\frac{QY_X}{QY_{ST}} = \frac{1.41}{2.56} \quad (7.27)$$

The assumption used in the comparative method is valid only in the Beer-Lambert law linear regime. Beer-Lambert law states that absorbance is directly proportional to the path length of light travelled within the sample, and concentration of the sample. The factors that affect the quantum yield measurements are the following:

- **Concentration** – Low concentrations should be used (absorbance < 0.2 a.u.) to avoid effects such as self quenching.
- **Solvent** – It is important to take into account the solvents used for the test and standard solutions. If the solvents used for both are the same then the comparison is trivial. However, if the solvents in the test and standard solutions are different, this difference needs to be accounted for. This is done by incorporating the solvent refractive indices in the ratio calculation.

- **Standard samples** – The standard samples should be characterized thoroughly. In addition, the standard sample used should absorb at the excitation wavelength of the test sample.
- **Sample preparation** – It is important that the cuvettes used are clean, scratch free and clear on all four sides. The solvents used must be of spectroscopic grade and should not absorb in the wavelength range.
- **Slit width** – The slit widths for all measurements must be kept constant.

The quantum yield of the Group 12-16 semiconductor nanoparticles are affected by many factors such as the following.

- **Surface defects** – The surface defects of semiconductor quantum dots occur in the form of unsatisfied valencies. Thus resulting in unwanted recombinations. These unwanted recombinations reduce the loss of energy through radiative decay, and thus reducing the fluorescence.
- **Surface ligands** – If the surface ligand coverage is a 100%, there is a smaller chance of surface recombinations to occur.
- **Solvent polarity** – If the solvent and the ligand have similar solvent polarities, the nanoparticles are more dispersed, reducing the loss of electrons through recombinations.

7.4.4.4.2 Qualitative Information

Apart from quantum yield information, the relationship between intensity of fluorescence emission and wavelength, other useful qualitative information such as size distribution, shape of the particle and presence of surface defects can be obtained.

As shown in Figure 7.64, the shape of the plot of intensity versus wavelength is a Gaussian distribution. In Figure 7.64, the full width at half maximum (FWHM) is given by the difference between the two extreme values of the wavelength at which the photoluminescence intensity is equal to half its maximum value. From the full width half max (FWHM) of the fluorescence intensity Gaussian distribution, it is possible to determine qualitatively the size distribution of the sample. For a Group 12-16 quantum dot sample if the FWHM is greater than 30, the system is very polydisperse and has a large size distribution. It is desirable for all practical applications for the FWHM to be lesser than 30.

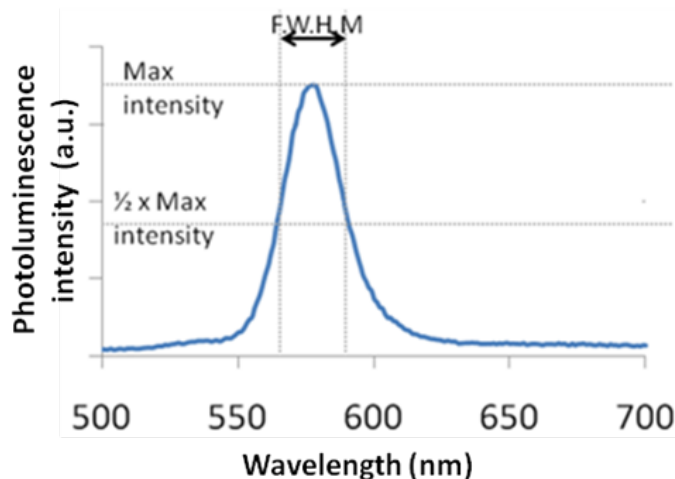


Figure 7.64: Emission spectra of CdSe QDs showing the full width half maximum (FWHM).

From the FWHM of the emission spectra, it is also possible to qualitatively get an idea if the particles are spherical or shaped. During the synthesis of the shaped particles, the thickness of the rod or the arm of the tetrapod does not vary among the different particles, as much as the length of the rods or arms changes. The thickness of the arm or rod is responsible for the quantum effects in shaped particles. In the case of quantum dots, the particle is quantum confined in all dimensions. Thus, any size distribution during the synthesis of quantum dots greatly affects the emission spectra. As a result the FWHM of rods and tetrapods is much smaller as compared to a quantum dot. Hence, qualitatively it is possible to differentiate between quantum dots and other shaped particles.

Another indication of branched structures is the decrease in the intensity of fluorescence peaks. Quantum dots have very high fluorescence values as compared to branched particles, since they are quantum confined in all dimensions as compared to just 1 or 2 dimensions in the case of branched particles.

7.4.4.5 Fluorescence spectra of different Group 12-16 semiconductor nanoparticles

The emission spectra of all Group 12-16 semiconductor nanoparticles are Gaussian curves as shown in Figure 7.62 and Figure 7.64. The only difference between them is the band gap energy, and hence each of the Group 12-16 semiconductor nanoparticles fluoresce over different ranges of wavelengths

7.4.4.5.1 Cadmium selenide

Since its bulk band gap (1.74 eV, 712 nm) falls in the visible region cadmium Selenide (CdSe) is used in various applications such as solar cells, light emitting diodes, etc. Size evolving emission spectra of cadmium selenide is shown in Figure 7.65. Different sized CdSe particles have different colored fluorescence spectra. Since cadmium and selenide are known carcinogens and being nanoparticles are easily absorbed into the human body, there is some concern regarding these particles. However, CdSe coated with ZnS can overcome all the harmful biological effects, making cadmium selenide nanoparticles one of the most popular 12-16 semiconductor nanoparticle.

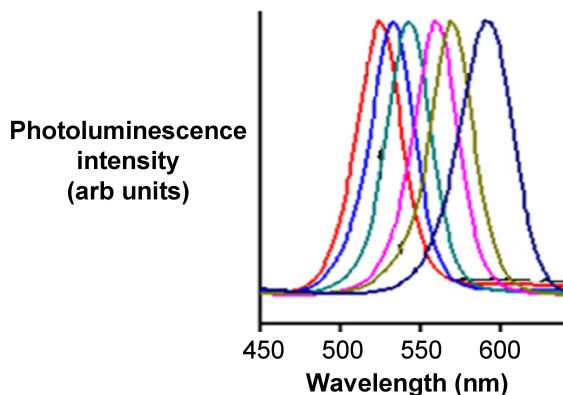


Figure 7.65: Size evolving CdSe emission spectra. Adapted from <http://www.physics.mq.edu.au>.

A combination of the absorbance and emission spectra is shown in Figure 7.66 for four different sized particles emitting green, yellow, orange, and red fluorescence.

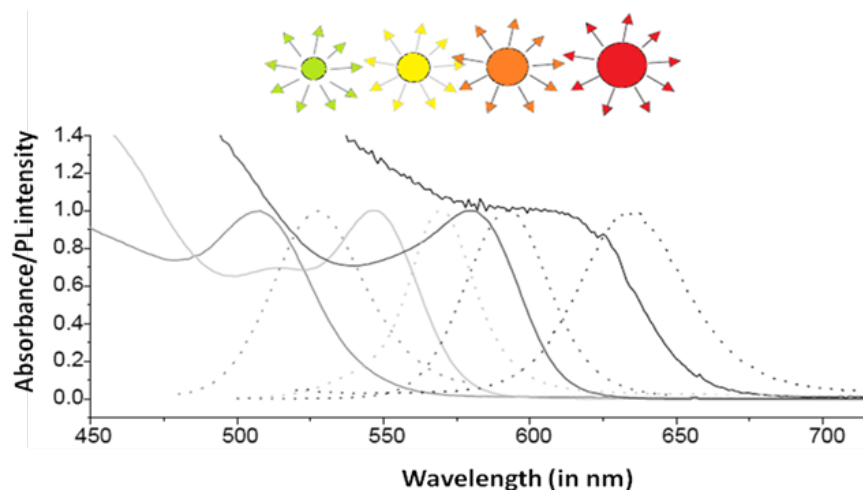


Figure 7.66: Absorption and emission spectra of CdSe quantum dots. Adapted from G. Schmid, *Nanoparticles: From Theory to Application*, Wiley-VCH, Weinham (2004).

7.4.4.5.2 Cadmium telluride

Cadmium Telluride (CdTe) has a band gap of 1.44 eV and thus absorbs in the infra red region. The size evolving CdTe emission spectra is shown in Figure 7.67.

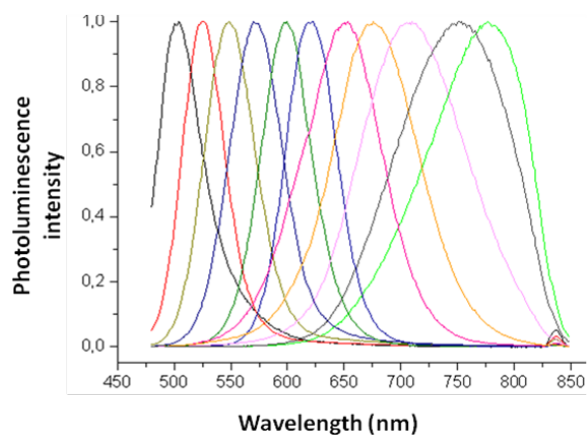


Figure 7.67: Size evolution spectra of CdTe quantum dots.

7.4.4.5.3 Adding shells to QDs

Capping a core quantum dot with a semiconductor material with a wider bandgap than the core, reduces the nonradiative recombination and results in brighter fluorescence emission. Quantum yields are affected by the presences of free surface charges, surface defects and crystal defects, which results in unwanted recombinations. The addition of a shell reduces the nonradiative transitions and majority of the electrons relax radiatively to the valence band. In addition, the shell also overcomes some of the surface defects.

For the CdSe-core/ZnS-shell systems exhibit much higher quantum yield as compared to core CdSe quantum dots as seen in Figure 7.68.

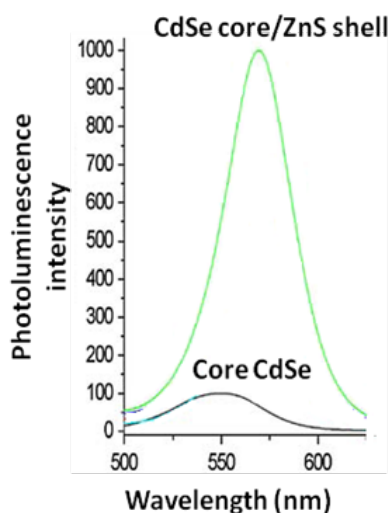


Figure 7.68: Emission spectra of core CdSe only and CdSe-core/ZnS-shell.

7.4.4.6 Bibliography

- A. T. R. Williams, S. A. Winfield, and J. N. Miller, *Analyst*, 1983, **108**, 1067.
- G. Schmid, *Nanoparticles: From Theory to Application*, Wiley-VCH, Weinham, (2004).
- J. Y. Hariba, *A Guide to Recording Fluorescence Quantum Yield*, Jobin Yvon Hariba Limited, Stanmore (2003).
- C. Qing Zhu, P. Wang, X. Wang, and Y. Li, *Nanoscale Res. Lett.*, 2008, **3**, 213.

7.5 Measuring the Specific Surface Area of Nanoparticle Suspensions using NMR¹²

7.5.1 Introduction

Surface area is a property of immense importance in the nano-world, especially in the area of heterogeneous catalysis. A solid catalyst works with its active sites binding to the reactants, and hence for a given active site

¹²This content is available online at <<http://cnx.org/content/m34663/1.1/>>.

reactivity, the higher the number of active sites available, the faster the reaction will occur. In heterogeneous catalysis, if the catalyst is in the form of spherical nanoparticles, most of the active sites are believed to be present on the outer surface. Thus it is very important to know the catalyst surface area in order to get a measure of the reaction time. One expresses this in terms of volume specific surface area, i.e., surface area/volume although in industry it is quite common to express it as surface area per unit mass of catalyst, e.g., m^2/g .

7.5.2 Overview of NMR

Nuclear magnetic resonance (NMR) is the study of the nuclei of the response of an atom to an external magnetic field. Many nuclei have a net magnetic moment with $I \neq 0$, along with an angular momentum in one direction where I is the spin quantum number of the nucleus. In the presence of an external magnetic field, a nucleus would precess around the field. With all the nuclei precessing around the external magnetic field, a measurable signal is produced.

NMR can be used on any nuclei with an odd number of protons or neutrons or both, like the nuclei of hydrogen (^1H), carbon (^{13}C), phosphorous (^{31}P), etc. Hydrogen has a relatively large magnetic moment ($\mu = 14.1 \times 10^{-27} \text{ J/T}$) and hence it is used in NMR logging and NMR rock studies. The hydrogen nucleus composes of a single positively charged proton that can be seen as a loop of current generating a magnetic field. It may be considered as a tiny bar magnet with the magnetic axis along the spin axis itself as shown in Figure 7.69. In the absence of any external forces, a sample with hydrogen alone will have the individual magnetic moments randomly aligned as shown in Figure 7.70.

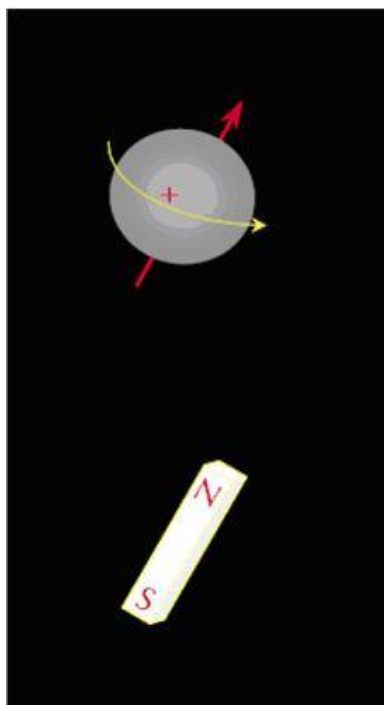


Figure 7.69: A simplistic representation of a spinning nucleus as bar magnet. Copyright: Halliburton Energy Services, Duncan, OK (1999).

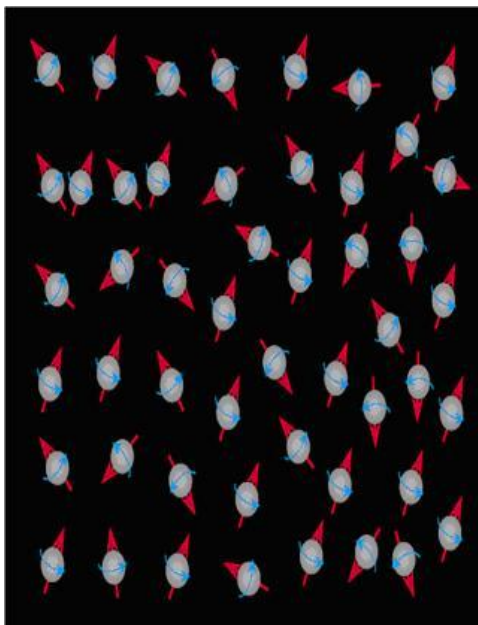


Figure 7.70: Representation of randomly aligned hydrogen nuclei. Copyright: Halliburton Energy Services, Duncan, OK (1999).

7.5.3 Advantages of NMR over BET technique

BET measurements follow the BET (Brunner-Emmet-Teller) adsorption isotherm of a gas on a solid surface. Adsorption experiments of a gas of known composition can help determine the specific surface area of the solid particle. This technique has been the main source of surface area analysis used industrially for a long time. However BET techniques take a lot of time for the gas-adsorption step to be complete while one shall see in the course of this module that NMR can give you results in times averaging around 30 minutes depending on the sample. BET also requires careful sample preparation with the sample being in dry powder form, whereas NMR can accept samples in the liquid state as well.

7.5.4 How does NMR work?

7.5.4.1 Polarization

Polarization involves the alignment of the individual magnetic nuclei in the presence of a static external magnetic field B_0 . This external field exerts a torque that forces the spinning nuclei to precess around it by a frequency given by the *Larmor frequency* given by (7.28), where γ is the gyromagnetic ratio which is a characteristic property of the nucleus. For hydrogen, $\gamma/2\pi = 42.58$ MHz/Tesla. This value is different for different elements.

$$f = \frac{\gamma B_0}{2\pi} \quad (7.28)$$

Considering the case of a proton under the influence of an external magnetic field, it will be in one of two possible energy states depending on the orientation of the precession axis. If the axis is parallel to B_0 , the

proton is in the lower energy state (preferred state) and in the higher energy state if anti-parallel shown by Figure 7.71.

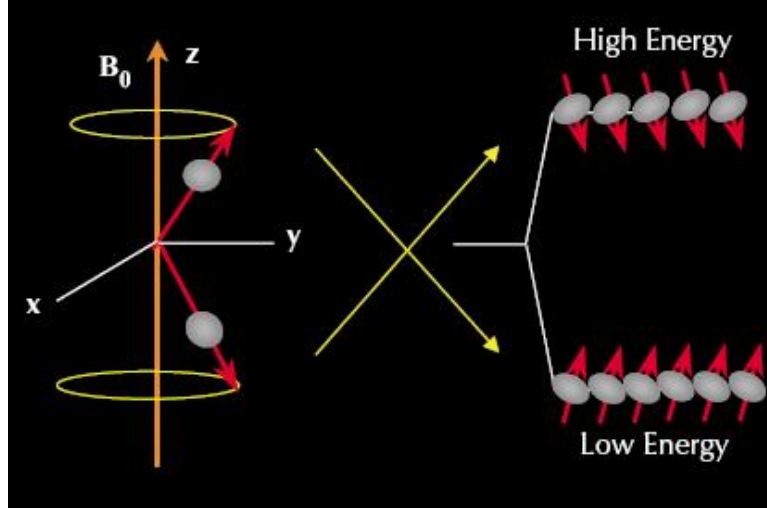


Figure 7.71: Alignment of precession axis. Copyright: Halliburton Energy Services, Duncan, OK (1999).

We define the net magnetization per unit volume of material, M_o , from Curie's law as (7.29), where N = number of protons, h = Planck's constant (6.626×10^{-34} Js), I = spin quantum number of the nucleus, k = Boltzmann's constant (1.381×10^{-23} m² Kg s⁻² K⁻¹), and T = temperature (K)

$$M_o = \frac{N\gamma^2 h^2 I(I+1) B_o}{12\pi^2 kT} \quad (7.29)$$

7.5.4.2 T_1 relaxation

The protons are said to be polarized completely once they are all aligned with the static external field. Polarization grows with a time constant called the *longitudinal relaxation time* (T_1) as shown in (7.30), where t = time of exposure to B_o , $M_z(t)$ = magnitude of magnetization at time t , with B_o along z -axis and T_1 = time at which $M_z(t)$ reaches 90% of its final value, i.e., M_o .

$$M_z(t) = M_o \left(1 - e^{-\frac{t}{T_1}}\right) \quad (7.30)$$

T_1 is the time at which $M_z(t)$ reaches 63% of its final value, M_o . A typical T_1 relaxation experiment involves application of a 90° RF pulse that rotates the magnetization to the transverse direction. With time, the magnetization returns to its original value in the same fashion described by the above equation.

Click on the video below to see the mechanism of T_1 relaxation

[MEDIA OBJECT]¹³

¹³This media object is a video file. Please view or download it at

<T1_Relaxation_Video.wmv>

T₁ relaxation mechanism.

7.5.4.3 T₂ Relaxation

Once the polarization is complete, the magnetization direction is tipped from the longitudinal plane to a transverse plane by applying an oscillating field B_1 perpendicular to B_0 . The frequency of B_1 must equal the Larmor frequency of the material from B_0 . This oscillating field causes a possible change in energy state, and in-phase precession. The total phenomenon is called *nuclear magnetic resonance* as shown in Figure 7.72.

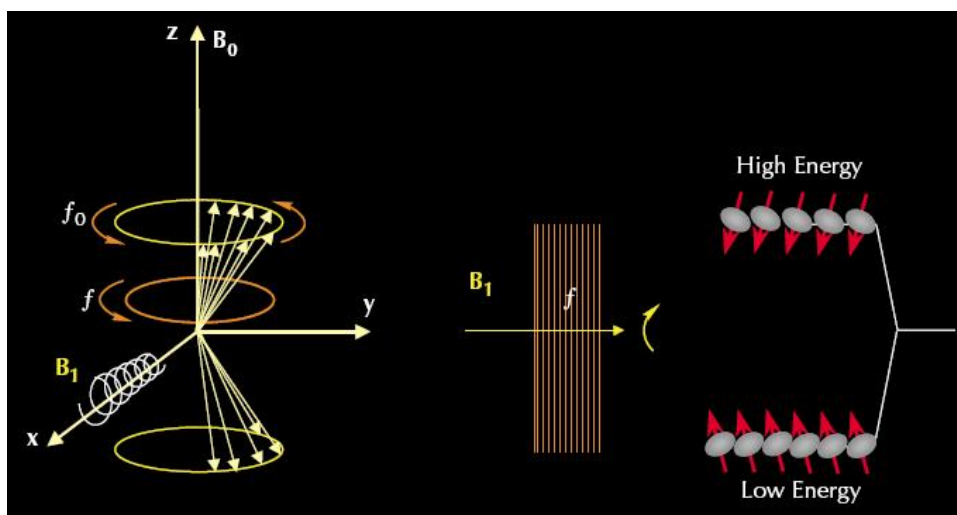


Figure 7.72: A schematic representation of the phenomenon of nuclear magnetic resonance. Copyright: Halliburton Energy Services, Duncan, OK (1999).

The oscillating field is generally pulsed in nature and so terms in books such as a 180° pulse or 90° pulse indicates the angle through which the net magnetization gets tipped over. Application of a 90° pulse causes precession in the transverse phase. When the field B_1 is removed, the nuclei begin to de-phase and the net magnetization decreases. Here a receiver coil detects the decaying signal in a process called *free induction decay (FID)*. This exponential decay has an FID time constant (T_2) which is in the order of microseconds.

The time constant of the transverse relaxation is referred as T_2 , and the amplitude of the decaying signal is given by (7.31), with symbols as defined earlier.

$$M_x(t) = M_0 e^{-\frac{t}{T_2}} \quad (7.31)$$

Click on the video below to see the mechanism of T_2 relaxation

[MEDIA OBJECT]¹⁴

T₂ relaxation mechanism.

¹⁴This media object is a video file. Please view or download it at

<T2_Relaxation_Video.wmv>

7.5.4.4 CPMG sequence

The de-phasing caused by T_1 relaxation can be reversed by applying a 180° pulse after a time τ has passed after application of the initial 90° pulse. Thus the phase of the transverse magnetization vector is now reversed by 180° so that “slower” vectors are now ahead of the “faster” vectors. These faster vectors eventually over-take the slower vectors and cause rephasing which is detected by a receiver coil as a *spin echo*. Thus time τ also passes between the application of the 180° pulse and the maximum peak in the spin echo. The entire sequence is illustrated in Figure 7.73. A single echo decays very quickly and hence a series of 180° pulses are applied repeatedly in a sequence called the *Carr-Purcell-Meiboom-Gill (CPMG) sequence*.

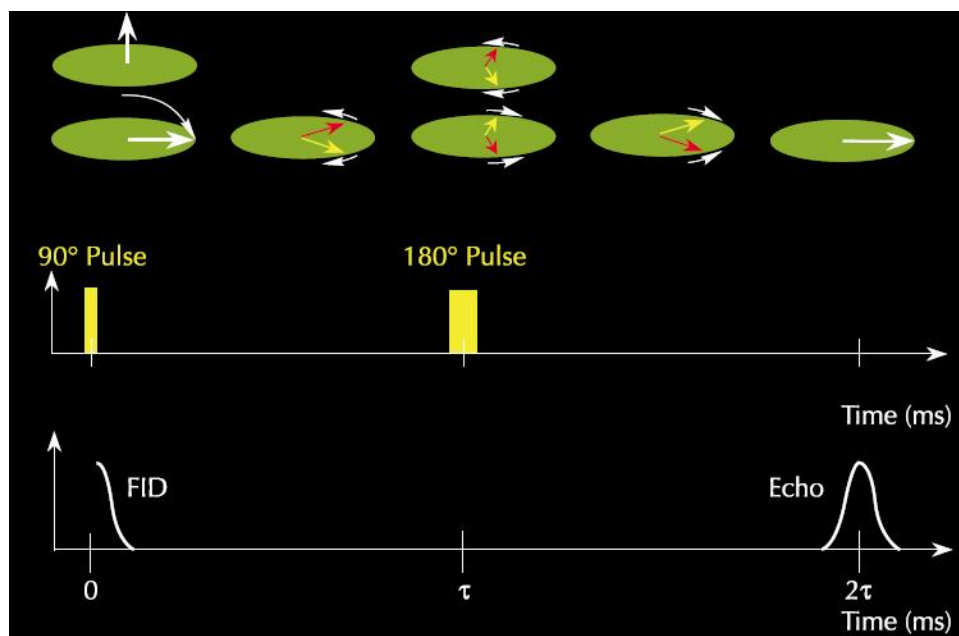


Figure 7.73: A schematic representation of the generation of a spin echo. Copyright: Halliburton Energy Services, Duncan, OK (1999).

7.5.5 NMR relaxation mechanism in solid suspensions

7.5.5.1 Calculations

From an atomic stand point, T_1 relaxation occurs when a precessing proton transfers energy with its surroundings as the proton relaxes back from higher energy state to its lower energy state. With T_2 relaxation, apart from this energy transfer there is also dephasing and hence T_2 is less than T_1 in general. For solid suspensions, there are three independent relaxation mechanisms involved:-

- 1) Bulk fluid relaxation, which affects both T_1 and T_2 relaxation.
- 2) Surface relaxation, which affects both T_1 and T_2 relaxation.
- 3) Diffusion in the presence of the magnetic field gradients, which affects only T_2 relaxation.

These mechanisms act in parallel so that the net effects are given by (7.32) and (7.33)

$$\frac{1}{T_2} = \frac{1}{T_{2,\text{bulk}}} + \frac{1}{T_{2,\text{surface}}} + \frac{1}{T_{2,\text{diffusion}}} \quad (7.32)$$

$$\frac{1}{T_1} = \frac{1}{T_{1,\text{bulk}}} + \frac{1}{T_{1,\text{surface}}} \quad (7.33)$$

The relative importance of each of these terms depend on the specific scenario. For the case of most solid suspensions in liquid, the diffusion term can be ignored by having a relatively uniform external magnetic field that eliminates magnetic gradients. Theoretical analysis has shown that the surface relaxation terms can be written as (7.34) and (7.35), where ρ = surface relaxivity and s/v = specific surface area.

$$\frac{1}{T_{1,\text{surface}}} = \rho_1 \left(\frac{S}{V} \right)_{\text{particle}} \quad (7.34)$$

$$\frac{1}{T_{2,\text{surface}}} = \rho_2 \left(\frac{S}{V} \right)_{\text{particle}} \quad (7.35)$$

Thus one can use T_1 or T_2 relaxation experiment to determine the specific surface area. We shall explain the case of the T_2 technique further as (7.36).

$$\frac{1}{T_2} = \frac{1}{T_{2,\text{bulk}}} + \rho_2 \left(\frac{S}{V} \right)_{\text{particle}} \quad (7.36)$$

One can determine T_2 by spin-echo measurements for a series of samples of known S/V values and prepare a calibration chart as shown in Figure 7.74, with the intercept as $\frac{1}{T_{2,\text{bulk}}}$ and the slope as ρ_2 , one can thus find the specific surface area of an unknown sample of the same material.

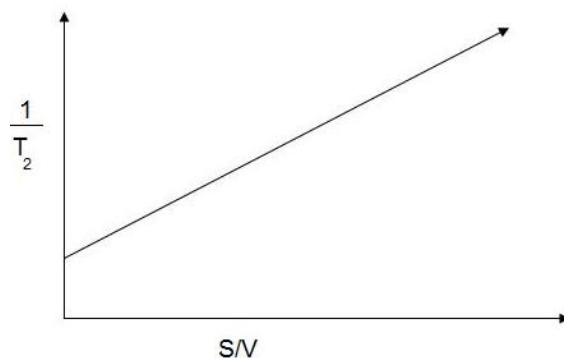


Figure 7.74: Example of a calibration plot of $1/T_2$ versus specific surface area (S/V) of a sample.

7.5.6 Sample preparation and experimental setup

The sample must be soluble in the solvent. For proton NMR, about 0.25-1.00 mg/mL are needed depending on the sensitivity of the instrument.

NOTE: The solvent properties will have an impact of some or all of the spectrum. Solvent viscosity affects obtainable resolution, while other solvents like water or ethanol have exchangeable protons that will prevent the observation of such exchangeable protons present in the solute itself. Solvents must be chosen such that the temperature dependence of solute solubility is low in the operation temperature range. Solvents containing aromatic groups like benzene can cause shifts in the observed spectrum compared to non-aromatic solvents.

NMR tubes are available in a wide range of specifications depending on specific scenarios. The tube specifications need to be extremely narrow while operating with high strength magnetic fields. The tube needs to be kept extremely clean and free from dust and scratches to obtain good results, irrespective of the quality of the tube. Tubes can be cleaned without scratching by rinsing out the contents and soaking them in a degreasing solution, and by avoiding regular glassware cleaning brushes. After soaking for a while, rinse with distilled water and acetone and dry the tube by blowing filtered nitrogen gas through a pipette or by using a swab of cotton wool.

Filter the sample solution by using a Pasteur pipette stuffed with a piece of cotton wool at the neck. Any suspended material like dust can cause changes in the spectrum. When working with dilute aqueous solutions, sweat itself can have a major effect and so gloves are recommended at all times.

NOTE: Sweat contains mainly water, minerals (sodium 0.9 g/L, potassium 0.2 g/L, calcium 0.015 g/L, magnesium 0.0013 g/L and other trace elements like iron, nickel, zinc, copper, lead and chromium), as well as lactate and urea. In presence of a dilute solution of the sample, the proton-containing substances in sweat (e.g., lactate and urea) can result in a large signal that can mask the signal of the sample.

The NMR probe is the most critical piece of equipment as it contains the apparatus that must detect the small NMR signals from the sample without adding a lot of noise. The size of the probe is given by the diameter of the NMR tube it can accommodate with common sizes 5, 10 and 15 mm. A larger size probe can be used in the case of less sensitive samples in order to get as much solute into the active zone as possible. When the sample is available in less quantity, use a smaller size tube to get an intrinsically higher sensitivity.

7.5.6.1 NMR analysis

A result sheet of T_2 relaxation has the plot of magnetization versus time, which will be linear in a semi-log plot as shown in Figure 7.75. Fitting it to the equation, we can find T_2 and thus one can prepare a calibration plot of $1/T_2$ versus S/V of known samples.

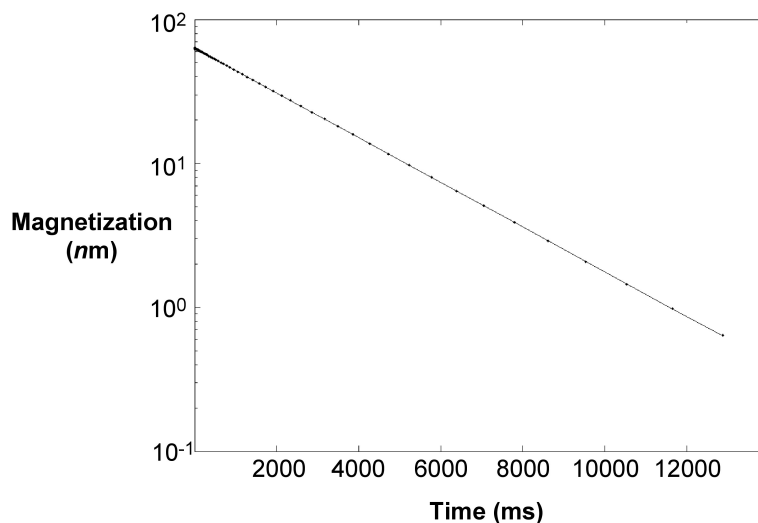


Figure 7.75: Example of T_2 relaxation with magnetization versus time on a semi-log plot.

7.5.6.2 Limitations of the T_2 technique

The following are a few of the limitations of the T_2 technique:

- One can't always guarantee no magnetic field gradients, in which case the T_1 relaxation technique is to be used. However this takes much longer to perform than the T_2 relaxation.
- There is the requirement of the odd number of nucleons in the sample or solvent.
- The solid suspension should not have any para- or ferromagnetic substance (for instance, organics like hexane tend to have dissolved O_2 which is paramagnetic).
- The need to prepare a calibration chart of the material with known specific surface area.

7.5.6.3 Example of usage

A study of colloidal silica dispersed in water provides a useful example. Figure 7.76 shows a representation of an individual silica particle.

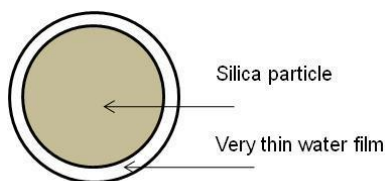


Figure 7.76: A representation of the silica particle with a thin water film surrounding it.

A series of dispersion in DI water at different concentrations was made and surface area calculated. The T_2 relaxation technique was performed on all of them with a typical T_2 plot shown in Figure 7.77 and T_2 was recorded at 2117 milliseconds for this sample.

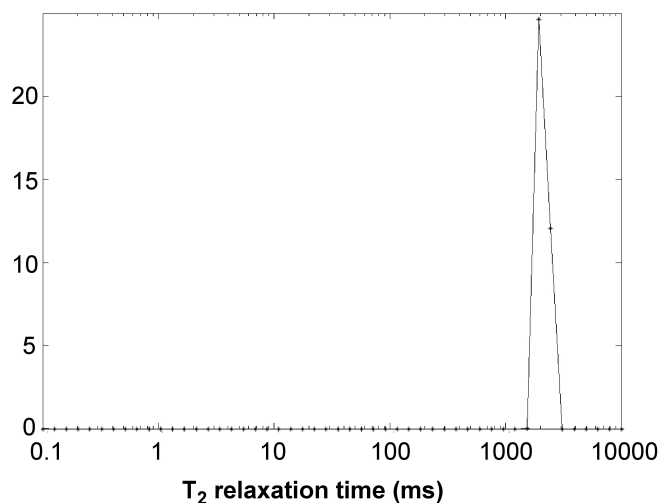


Figure 7.77: T_2 measurement for 2.3 wt% silica in DI water.

A calibration plot was prepared with $1/T_2 - 1/T_{2,\text{bulk}}$ as ordinate (the y-axis coordinate) and S/V as abscissa (the x-axis coordinate). This is called the *surface relaxivity plot* and is illustrated in Figure 7.78.

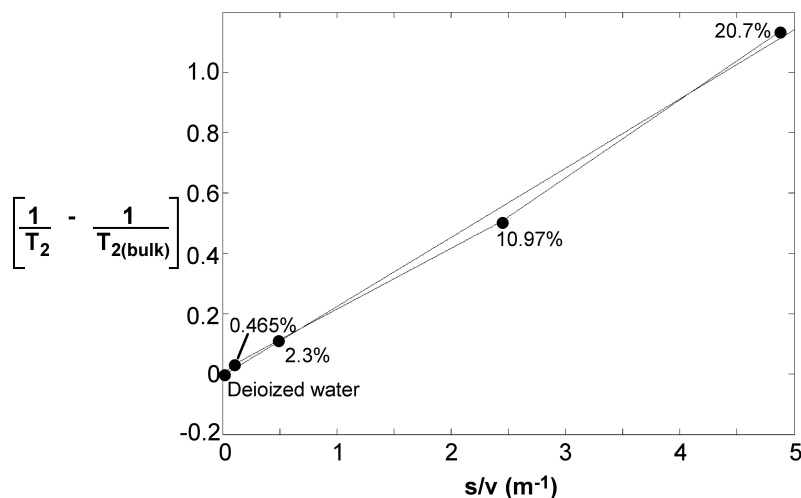


Figure 7.78: Calibration plot of $(1/T_2 - 1/T_{2,\text{Bulk}})$ versus specific surface area for silica in DI water.

Accordingly for the colloidal dispersion of silica in DI water, the best fit resulted in (7.37), from which one can see that the value of surface relaxivity, 2.3×10^{-8} , is in close accordance with values reported in literature.

$$\frac{1}{T_2} - \frac{1}{T_{2,\text{bulk}}} = 2.3 \times 10^{-8} \left(\frac{S}{V} \right) - 0.0051 \quad (7.37)$$

The T_2 technique has been used to find the pore-size distribution of water-wet rocks. Information of the pore size distribution helps petroleum engineers model the permeability of rocks from the same area and hence determine the extractable content of fluid within the rocks.

Usage of NMR for surface area determination has begun to take shape with a company, Xigo nanotools, having developed an instrument called the Acorn AreaTM to get surface area of a suspension of aluminum oxide. The results obtained from the instrument match closely with results reported by other techniques in literature. Thus the T_2 NMR technique has been presented as a strong case to obtain specific surface areas of nanoparticle suspensions.

7.5.7 Bibliography

- G. R Coates, L. Xiao, and M.G. Prammer, *NMR Logging: Principles & Applications*, Halliburton Energy Services, Houston (2001).
- B. Cowan, *Nuclear magnetic resonance and relaxation*, Cambridge University Press, Cambridge UK (2001).
- W. E. Kenyon, *The Log Analyst*, 1997, **6**, 2.
- A. E. Derome, *Modern NMR Techniques for Chemistry Research*, Vol 6, Pergamon Press, Oxford (1988).

7.6 Characterization of Graphene by Raman Spectroscopy ¹⁵

7.6.1 Introduction

Graphene is a quasi-two-dimensional material, which comprises layers of carbon atoms arranged in six-member rings (Figure 7.79). Since being discovered by Andre Geim and co-workers at the University of Manchester, graphene has become one of the most exciting topics of research because of its distinctive band structure and physical properties, such as the observation of a quantum hall effect at room temperature, a tunable band gap, and a high carrier mobility.

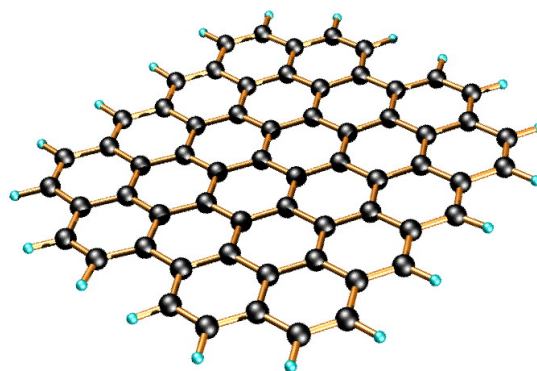


Figure 7.79: Idealized structure of a single graphene sheet.

Graphene can be characterized by many techniques including atomic force microscopy (AFM), transmission electron microscopy (TEM) and Raman spectroscopy. AFM can be used to determine the number of the layers of the graphene, and TEM images can show the structure and morphology of the graphene sheets. In many ways, however, Raman spectroscopy is a much more important tool for the characterization of graphene. First of all, Raman spectroscopy is a simple tool and requires little sample preparation. What's more, Raman spectroscopy can not only be used to determine the number of layers, but also can identify if the structure of graphene is perfect, and if nitrogen, hydrogen or other functionalization is successful.

7.6.2 Raman spectrum of graphene

While Raman spectroscopy is a useful technique for characterizing sp^2 and sp^3 hybridized carbon atoms, including those in graphite, fullerenes, carbon nanotubes, and graphene. Single, double, and multi-layer graphenes have also been differentiated by their Raman fingerprints.

shows a typical Raman spectrum of N-doped single-layer graphene. The D-mode, appears at approximately 1350 cm^{-1} , and the G-mode appears at approximately 1583 cm^{-1} . The other Raman modes are at 1620 cm^{-1} (D'-mode), 2680 cm^{-1} (2D-mode), and 2947 cm^{-1} (D+G-mode).

¹⁵This content is available online at <<http://cnx.org/content/m34667/1.2/>>.

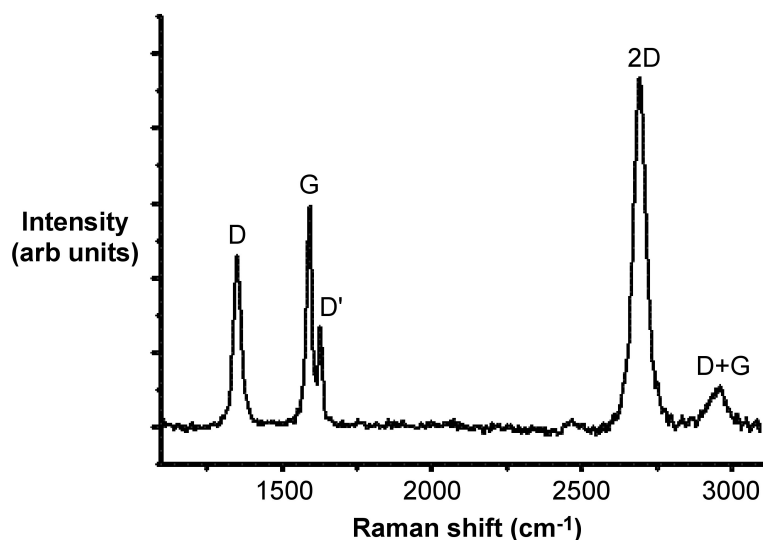


Figure 7.80: Raman spectrum with a 514.5 nm excitation laser wavelength of N-doped single-layer graphene.

7.6.2.1 The G-band

The G-mode is at about 1583 cm^{-1} , and is due to E_{2g} mode at the Γ -point. G-band arises from the stretching of the C-C bond in graphitic materials, and is common to all sp^2 carbon systems. The G-band is highly sensitive to strain effects in sp^2 system, and thus can be used to probe modification on the flat surface of graphene.

7.6.2.2 Disorder-induced D- band and D'- band

The D-mode is caused by disordered structure of graphene. The presence of disorder in sp^2 -hybridized carbon systems results in resonance Raman spectra, and thus makes Raman spectroscopy one of the most sensitive techniques to characterize disorder in sp^2 carbon materials. As is shown by a comparison of and , there is no D peak in the Raman spectra of graphene with a perfect structure.

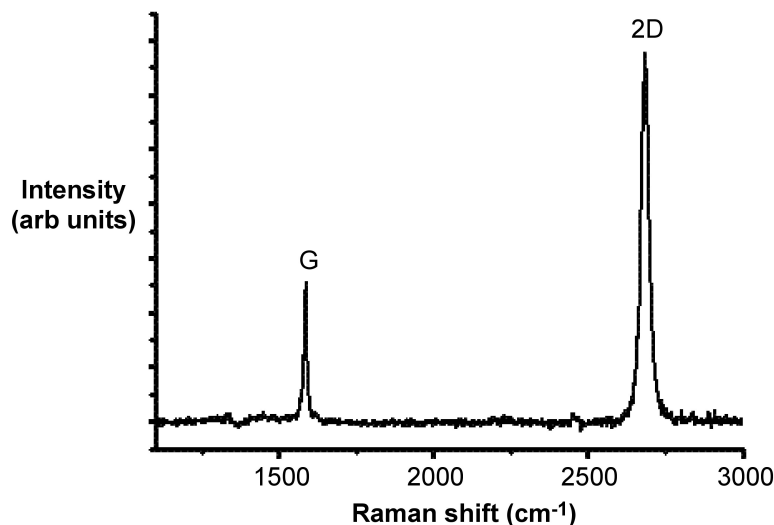


Figure 7.81: Raman spectrum with a 514.5 nm excitation laser wavelength of pristine single-layer graphene.

If there are some randomly distributed impurities or surface charges in the graphene, the G-peak can split into two peaks, G-peak (1583 cm^{-1}) and D'-peak (1620 cm^{-1}). The main reason is that the localized vibrational modes of the impurities can interact with the extended phonon modes of graphene resulting in the observed splitting.

7.6.2.3 The 2D-band

All kinds of sp^2 carbon materials exhibit a strong peak in the range $2500 - 2800\text{ cm}^{-1}$ in the Raman spectra. Combined with the G-band, this spectrum is a Raman signature of graphitic sp^2 materials and is called 2D-band. 2D-band is a second-order two-phonon process and exhibits a strong frequency dependence on the excitation laser energy.

What's more, the 2D band can be used to determine the number of layer of graphene. This is mainly because in the multi-layer graphene, the shape of 2D band is pretty much different from that in the single-layer graphene. As shown in , the 2D band in the single-layer graphene is much more intense and sharper as compared to the 2D band in multi-layer graphene.

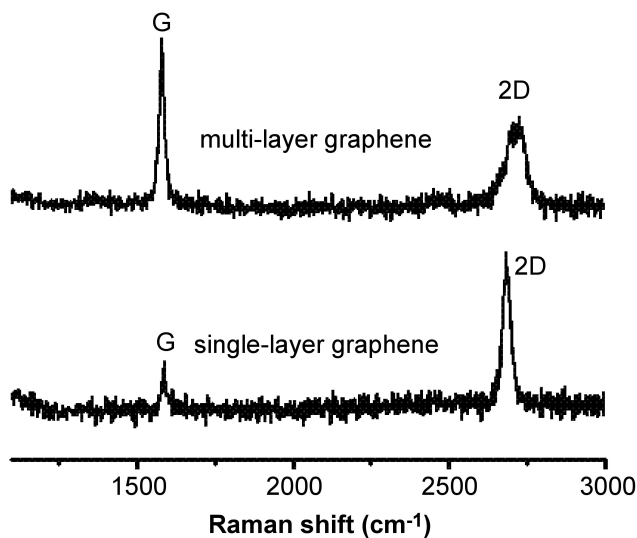


Figure 7.82: Raman spectrum with a 514.5 nm excitation laser wavelength of pristine single-layer and multi-layer graphene.

7.6.3 Bibliography

- G. G. Chen, P. Joshi, S. Tadigadapa, and P. C. Eklund, *Nano Lett.*, 2006, **6**, 2667.
- C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, and S. Roth, A. K. Geim, *Phys. Rev. Lett.*, 2006, **97**, 187401.
- M. A. Pimenta, G. Dresselhaus, M. S. Dresselhaus, L. A. Cancado, A. Jorio, and R. Sato, *Phys. Chem. Chem. Phys.*, 2007, **9**, 1276.

Chapter 8

Surface Morphology and Structure

8.1 The Application of VSI (Vertical Scanning Interferometry) to the Study of Crystal Surface Processes ¹

8.1.1 Introduction

The processes which occur at the surfaces of crystals depend on many external and internal factors such as crystal structure and composition, conditions of a medium where the crystal surface exists and others. The appearance of a crystal surface is the result of complexity of interactions between the crystal surface and the environment. The mechanisms of surface processes such as dissolution or growth are studied by the physical chemistry of surfaces. There are a lot of computational techniques which allows us to predict the changing of surface morphology of different minerals which are influenced by different conditions such as temperature, pressure, pH and chemical composition of solution reacting with the surface. For example, Monte Carlo method is widely used to simulate the dissolution or growth of crystals. However, the theoretical models of surface processes need to be verified by natural observations. We can extract a lot of useful information about the surface processes through studying the changing of crystal surface structure under influence of environmental conditions. The changes in surface structure can be studied through the observation of crystal surface topography. The topography can be directly observed macroscopically or by using microscopic techniques. Microscopic observation allows us to study even very small changes and estimate the rate of processes by observing changing the crystal surface topography in time.

Much laboratory worked under the reconstruction of surface changes and interpretation of dissolution and precipitation kinetics of crystals. Invention of AFM made possible to monitor changes of surface structure during dissolution or growth. However, to detect and quantify the results of dissolution processes or growth it is necessary to determine surface area changes over a significantly larger field of view than AFM can provide. More recently, vertical scanning interferometry (VSI) has been developed as new tool to distinguish and trace the reactive parts of crystal surfaces. VSI and AFM are complementary techniques and practically well suited to detect surface changes.

VSI technique provides a method for quantification of surface topography at the angstrom to nanometer level. Time-dependent VSI measurements can be used to study the surface-normal retreat across crystal and other solid surfaces during dissolution process. Therefore, VSI can be used to directly and nondirectly measure mineral dissolution rates with high precision. Analogically, VSI can be used to study kinetics of crystal growth.

¹This content is available online at <<http://cnx.org/content/m22326/1.4/>>.

8.1.2 Physical principles of optical interferometry

Optical interferometry allows us to make extremely accurate measurements and has been used as a laboratory technique for almost a hundred years. Thomas Young observed interference of light and measured the wavelength of light in an experiment, performed around 1801. This experiment gave an evidence of Young's arguments for the wave model for light. The discovery of interference gave a basis to development of interferometry techniques widely successfully used as in microscopic investigations, as in astronomic investigations.

The physical principles of optical interferometry exploit the wave properties of light. Light can be thought as electromagnetic wave propagating through space. If we assume that we are dealing with a linearly polarized wave propagating in a vacuum in z direction, electric field E can be represented by a sinusoidal function of distance and time.

$$E(x, y, z, t) = a \cos[2\pi(vt - z/\lambda)] \quad (8.1)$$

Where a is the amplitude of the light wave, v is the frequency, and λ is its wavelength. The term within the square brackets is called the phase of the wave. Let's rewrite this equation in more compact form,

$$E(x, y, z, t) = a \cos[\omega t - kz] \quad (8.2)$$

where $\omega = 2\pi v$ is the circular frequency, and $k = 2\pi/\lambda$ is the propagation constant. Let's also transform this second equation into a complex exponential form,

$$E(x, y, z, t) = \text{Re}\{a \exp(i\varphi) \exp(i\omega t)\} = \text{Re}\{A \exp(i\omega t)\} \quad (8.3)$$

where $\varphi = 2\pi z/\lambda$ and $A = \exp(-i\varphi)$ is known as the complex amplitude. If n is a refractive index of a medium where the light propagates, the light wave traverses a distance d in such a medium. The equivalent optical path in this case is

$$p = n \cdot d \quad (8.4)$$

When two light waves are superposed, the result intensity at any point depends on whether reinforce or cancel each other (Figure 8.1). This is well known phenomenon of interference. We will assume that two waves are propagating in the same direction and are polarized with their field vectors in the same plane. We will also assume that they have the same frequency. The complex amplitude at any point in the interference pattern is then the sum of the complex amplitudes of the two waves, so that we can write,

$$A = A_1 + A_2 \quad (8.5)$$

where $A_1 = a_1 \exp(-i\varphi_1)$ and $A_2 = a_2 \exp(-i\varphi_2)$ are the complex amplitudes of two waves. The resultant intensity is, therefore,

$$I = |A|^2 = I_1 + I_2 + 2(I_1 I_2)^{1/2} \cos \Delta\varphi \quad (8.6)$$

where I_1 and I_2 are the intensities of two waves acting separately, and $\Delta\varphi = \varphi_1 - \varphi_2$ is the phase difference between them. If the two waves are derived from a common source, the phase difference corresponds to an optical path difference,

$$\Delta p = (\lambda/2\pi) \Delta\varphi \quad (8.7)$$

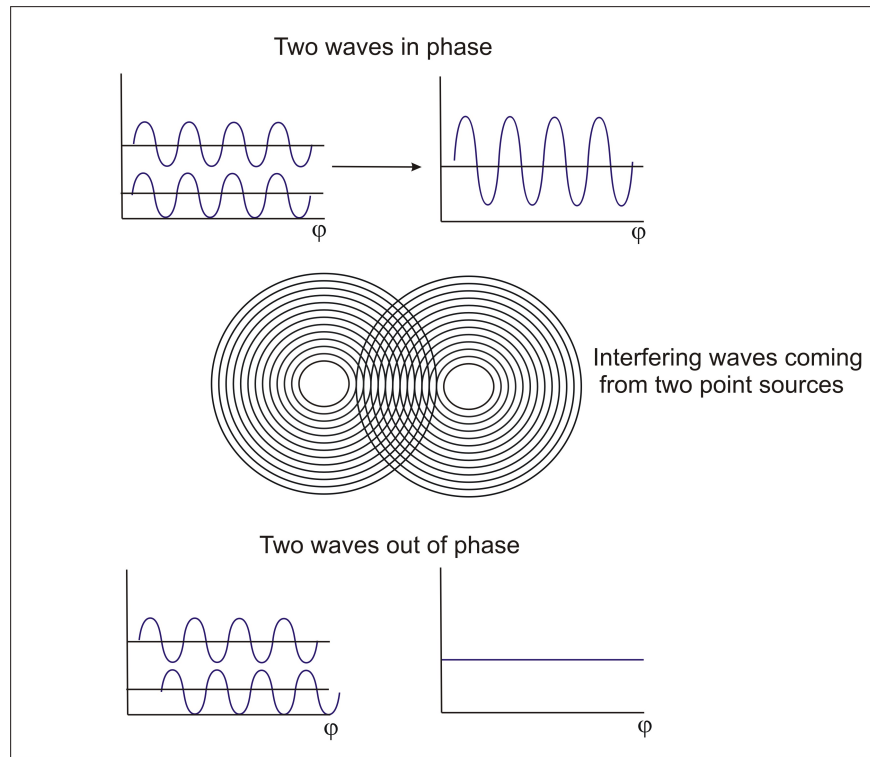


Figure 8.1: The scheme of interferometric wave interaction when two waves interact with each other, the amplitude of resulting wave will increase or decrease. The value of this amplitude depends on phase difference between two original waves.

If $\Delta\varphi$, the phase difference between the beams, varies linearly across the field of view, the intensity varies sinusoidally, giving rise to alternating light and dark bands or fringes (Figure 8.1). The intensity in an interference pattern has its maximum value

$$I_{\max} = I_1 + I_2 + 2(I_1 I_2)^{1/2} \quad (8.8)$$

when $\Delta\varphi = 2m\pi$, where m is an integer and its minimum value

$$I_{\min} = I_1 + I_2 - 2(I_1 I_2)^{1/2} \quad (8.9)$$

when $\Delta\varphi = (2m + 1)\pi$.

The principle of interferometry is widely used to develop many types of interferometric set ups. One of the earliest set ups is Michelson interferometry. The idea of this interferometry is quite simple: interference fringes are produced by splitting a beam of monochromatic light so that one beam strikes a fixed mirror and the other a movable mirror. An interference pattern results when the reflected beams are brought back together. The Michelson interferometric scheme is shown in Figure 8.2.

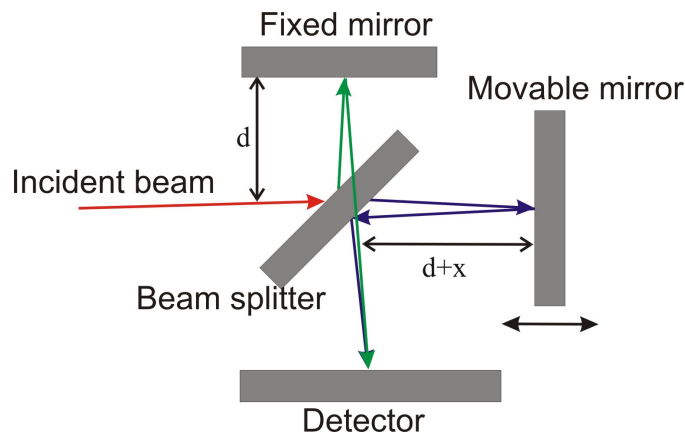


Figure 8.2: Schematic representation of a Michelson interferometry set-up.

The difference of path lengths between two beams is $2x$ because beams traverse the designated distances twice. The interference occurs when the path difference is equal to integer numbers of wavelengths,

$$\Delta p = 2x = m\lambda, m = 0, \pm 1, \pm 2 \dots \quad (8.10)$$

Modern interferometric systems are more complicated. Using special phase-measurement techniques they are capable of performing much more accurate height measurements than can be obtained just by directly looking at the interference fringes and measuring how they depart from being straight and equally spaced. Typically an interferometric system consists of a light source, beamsplitter, objective system, system of registration of signals and transformation into digital format and computer which processes data. Vertical scanning interferometry contains all these parts. Figure 8.3 shows a configuration of VSI interferometric system.

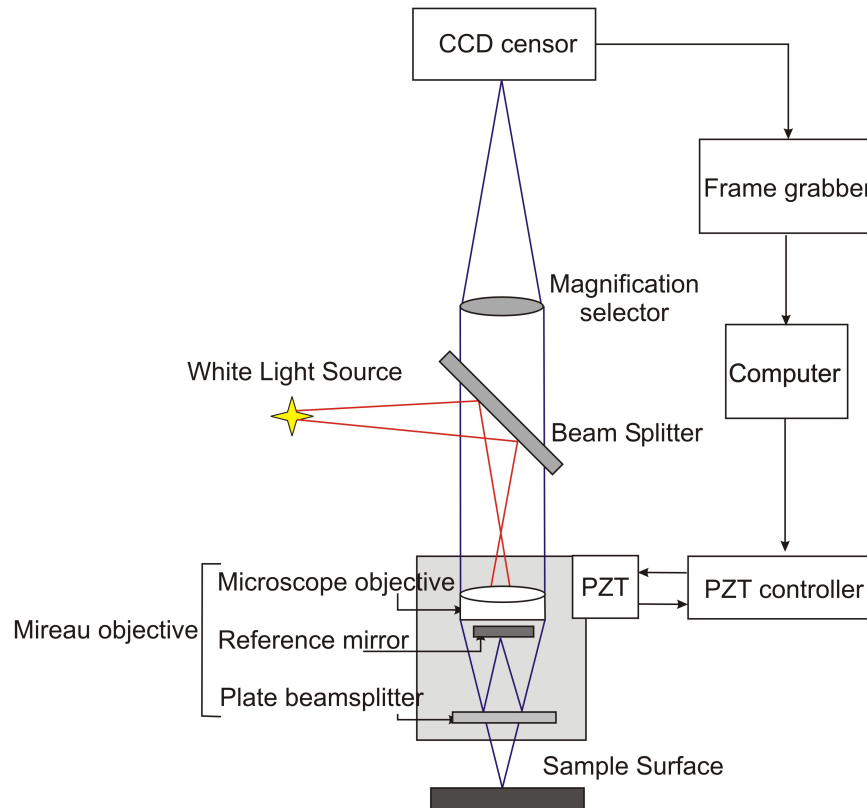


Figure 8.3: Schematic representation of the Vertical scanning interferometry (VSI) system.

Many of modern interferometric systems use Mirau objective in their constructions. Mireau objective is based on a Michelson interferometer. This objective consists of a lens, a reference mirror and a beamsplitter. The idea of getting interfering beams is simple: two beams (red lines) travel along the optical axis. Then they are reflected from the reference surface and the sample surface respectively (blue lines). After this these beams are recombined to interfere with each other. An illumination or light source system is used to direct light onto a sample surface through a cube beam splitter and the Mireau objective. The sample surface within the field of view of the objective is uniformly illuminated by those beams with different incidence angles. Any point on the sample surface can reflect those incident beams in the form of divergent cone. Similarly, the point on the reference symmetrical with that on the sample surface also reflects those illuminated beams in the same form.

The Mireau objective directs the beams reflected of the reference and the sample surface onto a CCD (charge-coupled device) sensor through a tube lens. The CCD sensor is an analog shift register that enables the transportation of analog signals (electric charges) through successive stages (capacitors), controlled by a clock signal. The resulting interference fringe pattern is detected by CCD sensor and the corresponding signal is digitized by a frame grabber for further processing with a computer.

The distance between a minimum and a maximum of the interferogram produced by two beams reflected from the reference and sample surface is known. That is, exactly half the wavelength of the light source. Therefore, with a simple interferogram the vertical resolution of the technique would be also limited to $\lambda/2$. If we will use a laser light as a light source with a wavelength of 300 nm the resolution would be only 150

nm. This resolution is not good enough for a detailed near-atomic scale investigation of crystal surfaces. Fortunately, the vertical resolution of the technique can be improved significantly by moving either the reference or the sample by a fraction of the wavelength of the light. In this way, several interferograms are produced. Then they are all overlayed, and their phase shifts compared by the computer software Figure 8.4. This method is widely known as phase shift interferometry (PSI).

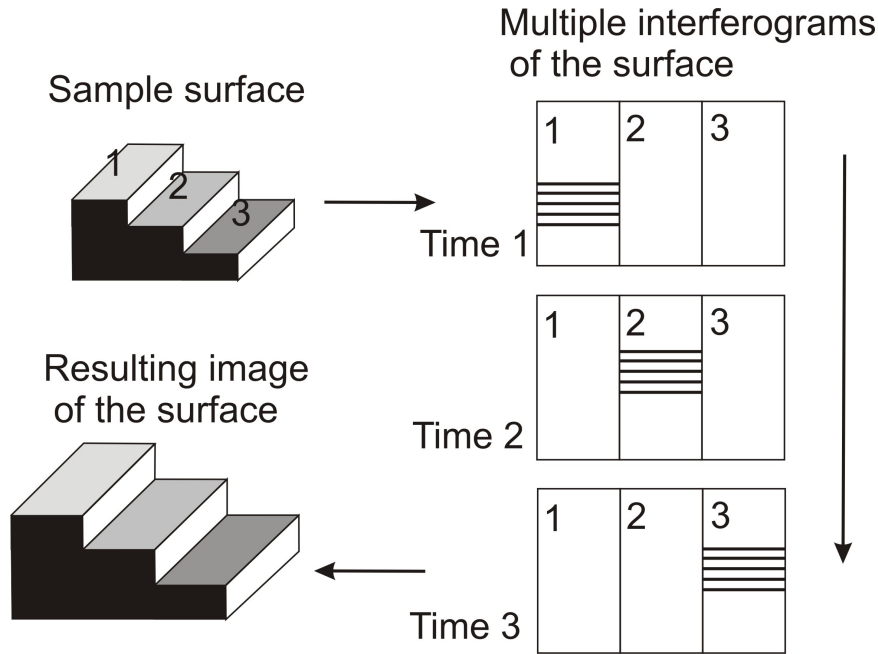


Figure 8.4: Sketch illustrating phase-shift technology. The sample is continuously moved along the vertical axes in order to scan surface topography. All interferograms are automatically overlayed using computer software.

Most optical testing interferometers now use phase-shifting techniques not only because of high resolution but also because phase-shifting is a high accuracy rapid way of getting the interferogram information into the computer. Also usage of this technique makes the inherent noise in the data taking process very low. As the result in a good environment angstrom or sub-angstrom surface height measurements can be performed. As it was said above, in phase-shifting interferometry the phase difference between the interfering beams is changed at a constant rate as the detector is read out. Once the phase is determined across the interference field, the corresponding height distribution on the sample surface can be determined. The phase distribution $\phi(x, y)$ is recorded by using the CCD camera.

Let's assign $A(x, y)$, $B(x, y)$, $C(x, y)$ and $D(x, y)$ to the resulting interference light intensities which are corresponded to phase-shifting steps of 0 , $\pi/2$, π and $3\pi/2$. These intensities can be obtained by moving the reference mirror through displacements of $\lambda/8$, $\lambda/4$ and $3\lambda/8$, respectively. The equations for the resulting intensities would be:

$$A(x, y) = I_1(x, y) + I_2(x, y) \cos \alpha(x, y) \quad (8.11)$$

$$B(x, y) = I_1(x, y) - I_2(x, y) \sin \alpha(x, y) \quad (8.12)$$

$$C(x, y) = I_1(x, y) - I_2(x, y) \cos \alpha(x, y) \quad (8.13)$$

$$D(x, y) = I_1(x, y) + I_2(x, y) \sin \alpha(x, y) \quad (8.14)$$

where $I_1(x, y)$ and $I_2(x, y)$ are two overlapping beams from two symmetric points on the test surface and the reference respectively. Solving equations (8.11)–(8.14), the phase map $\phi(x, y)$ of a sample surface will be given by the relation:

$$\varphi(x, y) = \frac{B(x, y) - D(x, y)}{A(x, y) - C(x, y)} \quad (8.15)$$

Once the phase is determined across the interference field pixel by pixel on a two-dimensional CCD array, the local height distribution/contour, $h(x, y)$, on the test surface is given by

$$h(x, y) = \frac{\lambda}{4\pi} \varphi(x, y) \quad (8.16)$$

Normally the resulted fringe can be in the form of a linear fringe pattern by adjusting the relative position between the reference mirror and sample surfaces. Hence any distorted interference fringe would indicate a local profile/contour of the test surface.

It is important to note that the Mireau objective is mounted on a capacitive closed-loop controlled PZT (piezoelectric actuator) as to enable phase shifting to be accurately implemented. The PZT is based on piezoelectric effect referred to the electric potential generated by applying pressure to piezoelectric material. This type of materials is used to convert electrical energy to mechanical energy and vice-versa. The precise motion that results when an electric potential is applied to a piezoelectric material has an importance for nanopositioning. Actuators using the piezo effect have been commercially available for 35 years and in that time have transformed the world of precision positioning and motion control.

Vertical scanning interferometer also has another name; white-light interferometry (WLI) because of using the white light as a source of light. With this type of source a separate fringe system is produced for each wavelength, and the resultant intensity at any point of examined surface is obtained by summing these individual patterns. Due to the broad bandwidth of the source the coherent length L of the source is short:

$$L = \frac{\lambda^2}{n\Delta\lambda} \quad (8.17)$$

where λ is the center wavelength, n is the refractive index of the medium, $\Delta\lambda$ is the spectral width of the source. In this way good contrast fringes can be obtained only when the lengths of interfering beams pathways are closed to each other. If we will vary the length of a pathway of a beam reflected from sample, the height of a sample can be determined by looking at the position for which a fringe contrast is a maximum. In this case interference pattern exist only over a very shallow depth of the surface. When we vary a pathway of sample-reflected beam we also move the sample in a vertical direction in order to get the phase at which maximum intensity of fringes will be achieved. This phase will be converted in height of a point at the sample surface.

The combination of phase shift technology with white-light source provides a very powerful tool to measure the topography of quite rough surfaces with the amplitude in heights about and the precision up to 1-2 nm. Through a developed software package for quantitatively evaluating the resulting interferogram, the proposed system can retrieve the surface profile and topography of the sample objects Figure 8.5.

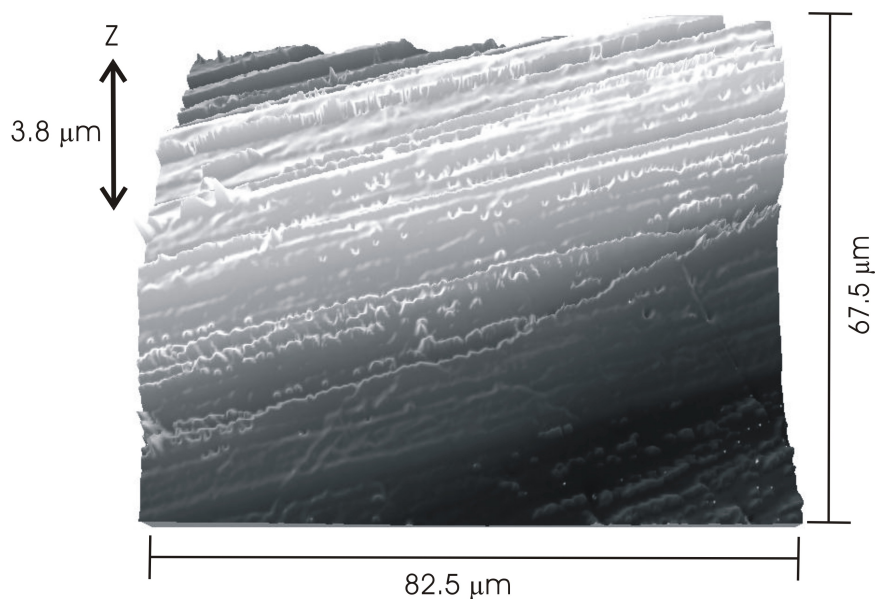


Figure 8.5: Example of muscovite surface topography, obtained by using VSI- 50x objective.

8.1.3 A comparison of common methods to determine surface topography: SEM, AFM and VSI

Except the interferometric methods described above, there are a several other microscopic techniques for studying crystal surface topography. The most common are scanning electron microscopy (SEM) and atomic force microscopy (AFM). All these techniques are used to obtain information about the surface structure. However they differ from each other by the physical principles on which they based.

8.1.3.1 Scanning electron microscopy

SEM allows us to obtain images of surface topography with the resolution much higher than the conventional light microscopes do. Also it is able to provide information about other surface characteristics such as chemical composition, electrical conductivity etc, see Figure 8.6. All types of data are generated by the reflecting of accelerated electron beams from the sample surface. When electrons strike the sample surface, they lose their energy by repeated random scattering and adsorption within an outer layer into the depth varying from 100 nm to 5 microns.

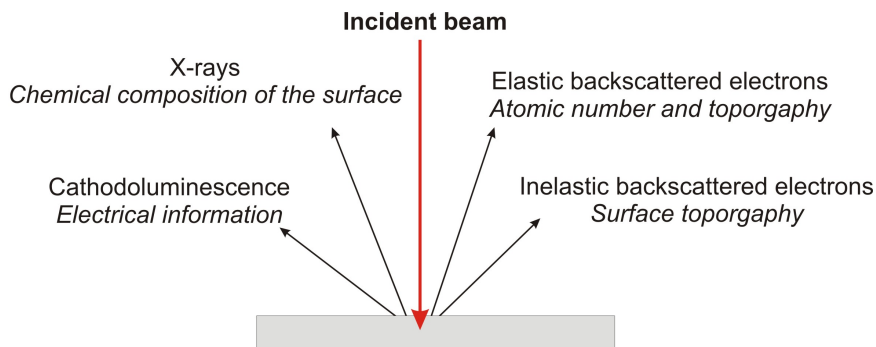


Figure 8.6: Scheme of electron beam-sample interaction at SEM analysis

The thickness of this outer layer also known as interactive layer depends on energy of electrons in the beam, composition and density of a sample. Result of the interaction between electron beam and the surface provides several types of signals. The main type is secondary or inelastic scattered electrons. They are produced as a result of interaction between the beam of electrons and weakly bound electrons in the conduction band of the sample. Secondary electrons are ejected from the k -orbitals of atoms within the surface layer of thickness about a few nanometers. This is because secondary electrons are low energy electrons (<50 eV), so only those formed within the first few nanometers of the sample surface have enough energy to escape and be detected. Secondary backscattered electrons provide the most common signal to investigate surface topography with lateral resolution up to 0.4 - 0.7 nm.

High energy beam electrons are elastic scattered back from the surface. This type of signal gives information about chemical composition of the surface because the energy of backscattered electrons depends on the weight of atoms within the interaction layer. Also this type of electrons can form secondary electrons and escape from the surface or travel farther into the sample than the secondary. The SEM image formed is the result of the intensity of the secondary electron emission from the sample at each x,y data point during the scanning of the surface.

8.1.3.2 Atomic force microscopy

AFM is a very popular tool to study surface dissolution. AFM set up consists of scanning a sharp tip on the end of a flexible cantilever which moves across a sample surface. The tips typically have an end radius of 2 to 20 nm, depending on tip type. When the tip touches the surface the forces of these interactions lead to deflection of a cantilever. The interaction between tip and sample surface involves mechanical contact forces, van der Waals forces, capillary forces, chemical bonding, electrostatic forces, magnetic forces etc. The deflection of a cantilever is usually measured by reflecting a laser beam off the back of the cantilever into a split photodiode detector. A schematic drawing of AFM can be seen in Figure 8.7. The two most commonly used modes of operation are contact mode AFM and tapping mode AFM, which are conducted in air or liquid environments.

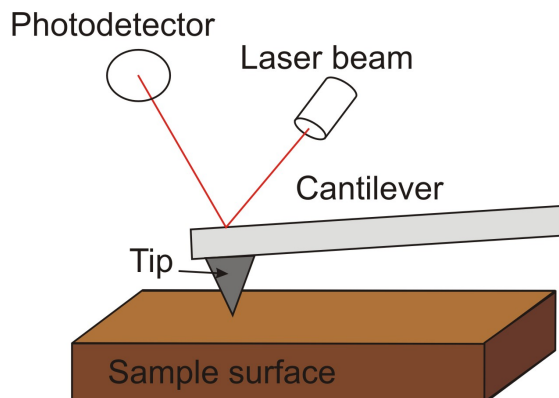


Figure 8.7: Schematic drawing of an AFM apparatus.

Working under the contact mode AFM scans the sample while monitoring the change in cantilever deflection with the split photodiode detector. Loop maintains a constant cantilever reflection by vertically moving the scanner to get a constant signal. The distance which the scanner goes by moving vertically at each x,y data point is stored by the computer to form the topographic image of the sample surface. Working under the tapping mode AFM oscillates the cantilever at its resonance frequency (typically ~ 300 kHz) and lightly “taps” the tip on the surface during scanning. The electrostatic forces increase when tip gets close to the sample surface, therefore the amplitude of the oscillation decreases. The laser deflection method is used to detect the amplitude of cantilever oscillation. Similar to the contact mode, feedback loop maintains a constant oscillation amplitude by moving the scanner vertically at every x,y data point. Recording this movement forms the topographical image. The advantage of tapping mode over contact mode is that it eliminates the lateral, shear forces present in contact mode. This enables tapping mode to image soft, fragile, and adhesive surfaces without damaging them while work under contact mode allows the damage to occur.

8.1.3.3 Comparison of techniques

All techniques described above are widely used in studying of surface nano- and micromorphology. However, each method has its own limitations and the proper choice of analytical technique depends on features of analyzed surface and primary goals of research.

All these techniques are capable to obtain an image of a sample surface with quite good resolution. The lateral resolution of VSI is much less, then for other techniques: 150 nm for VSI and 0.5 nm for AFM and SEM. Vertical resolution of AFM (0.5 Å) is better then for VSI (1 - 2 nm), however VSI is capable to measure a high vertical range of heights (1 mm) which makes possible to study even very rough surfaces. On the contrary, AFM allows us to measure only quite smooth surfaces because of its relatively small vertical scan range (7 μm). SEM has less resolution, than AFM because it requires coating of a conductive material with the thickness within several nm.

The significant advantage of VSI is that it can provide a large field of view ($845 \times 630 \mu\text{m}$ for 10x objective) of tested surfaces. Recent studies of surface roughness characteristics showed that the surface roughness parameters increase with the increasing field of view until a critical size of 250,000 μm is reached. This value is larger then the maximum field of view produced by AFM ($100 \times 100 \mu\text{m}$) but can be easily obtained by VSI. SEM is also capable to produce images with large field of view. However, SEM is able to provide only 2D images from one scan while AFM and VSI let us to obtain 3D images. It makes quantitative

analysis of surface topography more complicated, for example, topography of membranes is studied by cross section and top view images.

	VSI	AFM	SEM
Lateral resolution	0.5-1.2 μm	0.5 nm	0.5-1 nm
Vertical resolution	2 nm	0.5 Å	Only 2D images
Field of view	845 $\times$ 630 μm (10x objective)	100 $\times$ 100 μm	1-2 mm
Vertical range of scan	1 mm	10 μm	-
Preparation of a sample	-	-	Required coating of a conducted material
Required environment	Air	Air, liquid	Vacuum

Table 8.1: A comparison of VSI sample and resolution with AFM and SEM.

8.1.4 The experimental studying of surface processes using microscopic techniques

The limitations of each technique described above are critically important to choose appropriate technique for studying surface processes. Let's explore application of these techniques to study dissolution of crystals.

When crystalline matter dissolves the changes of the crystal surface topography can be observed by using microscopic techniques. If we will apply an unreactive mask (silicon for example) on crystal surface and place a crystalline sample into the experiment reactor then we get two types of surfaces: dissolving and remaining the same or unreacted. After some period of time the crystal surface starts to dissolve and change its z-level. In order to study these changes *ex situ* we can pull out a sample from the reaction cell then remove a mask and measure the average height difference $\Delta \bar{h}$ between the unreacted and dissolved areas. The average heights of dissolved and unreacted areas are obtained through digital processing of data obtained by microscopes. The velocity of normal surface retreat v_{SNR} during the time interval Δt is defined as

$$v_{\text{SNR}} = \frac{\Delta \bar{h}}{\Delta t}$$

Dividing this velocity by the molar volume $\bar{V}(\text{cm}^3/\text{mol})$ gives a global dissolution rate in the familiar units of moles per unit area per unit time:

$$R = \frac{v_{\text{SNR}}}{\bar{V}} \quad (8.18)$$

This method allows us to obtain experimental values of dissolution rates just by precise measuring of average surface heights. Moreover, using this method we can measure local dissolution rates at etch pits by monitoring changes in the volume and density of etch pits across the surface over time. VSI technique is capable to perform these measurements because of large vertical range of scanning. In order to get precise values of rates which are not depend on observing place of crystal surface we need to measure enough large areas. VSI technique provides data from areas which are large enough to study surfaces with heterogeneous dissolution dynamics and obtain average dissolution rates. Therefore, VSI makes possible to measure rates of normal surface retreat during the dissolution and observe formation, growth and distribution of etch pits on the surface.

However, if the mechanism of dissolution is controlled by dynamics of atomic steps and kink sites within a smooth atomic surface area, the observation of the dissolution process need to use a more precise technique. AFM is capable to provide information about changes in step morphology *in situ* when the dissolution

occurs. For example, immediate response of the dissolved surface to the changing of environmental conditions (concentrations of ions in the solution, pH etc.) can be studied by using AFM.

SEM is also used to examine micro and nanotexture of solid surfaces and study dissolution processes. This method allows us to observe large areas of crystal surface with high resolution which makes possible to measure a high variety of surfaces. The significant disadvantage of this method is the requirement to cover examine sample by conductive substance which limits the resolution of SEM. The other disadvantage of SEM is that the analysis is conducted in vacuum. Recent technique, environmental SEM or ESEM overcomes these requirements and makes possible even examine liquids and biological materials. The third disadvantage of this technique is that it produces only 2D images. This creates some difficulties to measure $\Delta\bar{h}$ within the dissolving area. One of advantages of this technique is that it is able to measure not only surface topography but also chemical composition and other surface characteristics of the surface. This fact is used to monitor changing in chemical composition during the dissolution.

8.1.5 Bibliography

- A. C. Lasaga, *Kinetic Theory in the Earth Sciences*. Princeton Univ. Press, Princeton, NJ (1998).
- A. Luttge, E. V. Bolton, and A. C. Lasaga A.C., *Am. J. Sci.*, 1999, **299**, 652.
- D. Kaczmarek, *Vacuum*, 2001, **62**, 303.
- P. Hariharan. *Optical interferometry*, Second edition, Academic press (2003) ISBN 0-12-311630-9.
- A. Luttge and P. G. Conrad, *Appl. Environ. Microbiol.*, 2004, **70**, 1627.
- A. C. Lasaga and A. Luttge, *American Mineralogist*, 2004, **89**, 527.
- K. J. Davis and A. Luttge, *Am. J. Sci.*, 2005, **305**, 727.
- S. H. Wang and Tay, *Meas. Sci. Technol.*, 2006, **17**, 617.
- A. Luttge and R. S. Arvidson, in *Kinetics of water-rock interaction*, Ed. S. Brantley, J. Kubicki, and A. White, Springer (2007).
- L. Zhang and A. Luttge, *American Mineralogist*, 2007, **92**, 1316.
- C. Fischer A. and Luttge, *Am. J. Sci.*, 2007, **307**, 955.
- Y. Wyart, G. Georges, C. Deumie, C. Amra, and P. Moulina, *J. Membrane Sci.*, 2008, **315**, 82.
- T. C. Vaimakis, E. D. Economou, and C. C. Trapalis, *J. Therm. Anal. Cal.*, 2008, **92**, 783.

8.2 Atomic Force Microscopy ²

8.2.1 Introduction

Atomic force microscopy (AFM) is a high-resolution form of scanning probe microscopy, also known as scanning force microscopy (SFM). The instrument uses a cantilever with a sharp tip at the end to scan over the sample surface (Figure 8.8). As the probe scans over the sample surface, attractive or repulsive forces between the tip and sample, usually in the form of van der Waal forces but also can be a number of others such as electrostatic and hydrophobic/hydrophilic, cause a deflection of the cantilever. The deflection is measured by a laser (Figure 8.8) which is reflected off the cantilever into photodiodes. As one of the photodiodes collects more light, it creates an output signal that is processed and provides information about the vertical bending of the cantilever. This data is then sent to a scanner that controls the height of the probe as it moves across the surface. The variance in height applied by the scanner can then be used to produce a three-dimensional topographical representation of the sample.

²This content is available online at <<http://cnx.org/content/m34664/1.1/>>.

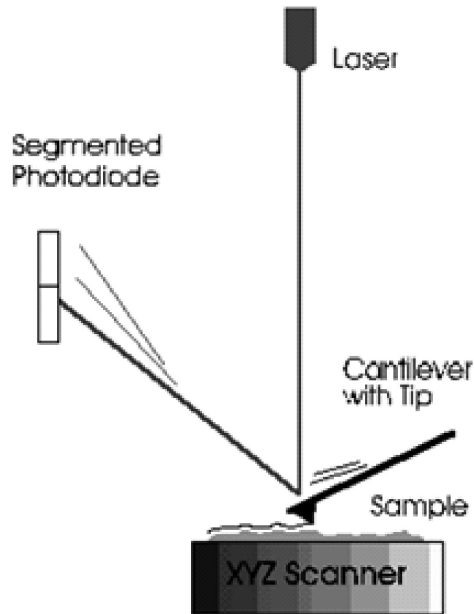


Figure 8.8: Simple schematic of atomic force microscope (AFM) apparatus. Adapted from H. G. Hansma, Department of Physics, University of California, Santa Barbara.

8.2.2 Modes of operation

8.2.2.1 Contact mode

The contact mode method utilizes a constant force for tip-sample interactions by maintaining a constant tip deflection (Figure 8.9). The tip communicates the nature of the interactions that the probe is having at the surface via feedback loops and the scanner moves the entire probe in order to maintain the original deflection of the cantilever. The constant force is calculated and maintained by using Hooke's Law, (8.19). This equation relates the force (F), spring constant (k), and cantilever deflection (x). Force constants typically range from 0.01 to 1.0 N/m. Contact mode usually has the fastest scanning times but can deform the sample surface. It is also only the only mode that can attain "atomic resolution."

$$F = -kx \quad (8.19)$$

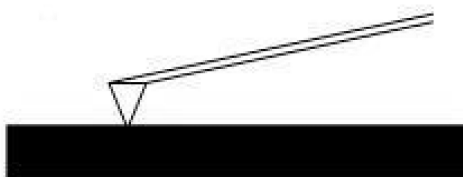


Figure 8.9: Schematic diagram of probe and surface interaction in contact mode.

8.2.2.2 Tapping mode

In the tapping mode the cantilever is externally oscillated at its fundamental resonance frequency (Figure 8.10). A piezoelectric on top of the cantilever is used to adjust the amplitude of oscillation as the probe scans across the surface. The deviations in the oscillation frequency or amplitude due to interactions between the probe and surface are measured, and provide information about the surface or types of material present in the sample. This method is gentler than contact AFM since the tip is not dragged across the surface, but it does require longer scanning times. It also tends to provide higher lateral resolution than contact AFM.

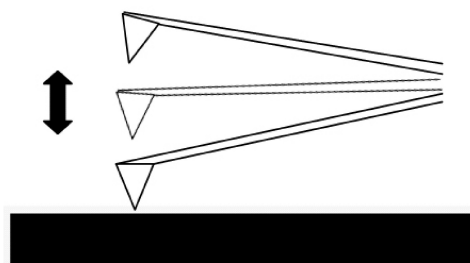


Figure 8.10: Diagram of probe and surface interaction in tapping mode.

8.2.2.3 Noncontact mode

For noncontact mode the cantilever is oscillated just above its resonance frequency and this frequency is decreased as the tip approaches the surface and experiences the forces associated with the material (Figure 8.11). The average tip-to-sample distance is measured as the oscillation frequency or amplitude is kept constant, which then can be used to image the surface. This method exerts very little force on the sample, which extends the lifetime of the tip. However, it usually does not provide very good resolution unless placed under a strong vacuum.

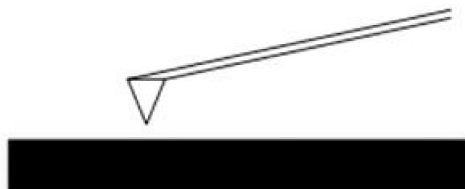


Figure 8.11: Diagram of probe and surface interaction in noncontact mode.

8.2.3 Experimental limitations

A common problem seen in AFM images is the presence of artifacts which are distortions of the actual topography, usually either due to issues with the probe, scanner, or image processing. The AFM scans slowly which makes it more susceptible to external temperature fluctuations leading to thermal drift. This leads to artifacts and inaccurate distances between topographical features.

It is also important to consider that the tip is not perfectly sharp and therefore may not provide the best aspect ratio, which leads to a convolution of the true topography. This leads to features appearing too large or too small since the width of the probe cannot precisely move around the particles and holes on the surface. It is for this reason that tips with smaller radii of curvature provide better resolution in imaging. The tip can also produce false images and poorly contrasted images if it is blunt or broken.

The movement of particles on the surface due to the movement of the cantilever can cause noise, which forms streaks or bands in the image. Artifacts can also be made by the tip being of inadequate proportions compared to the surface being scanned. It is for this reason that it is important to use the ideal probe for the particular application.

8.2.4 Sample size and preparation

The sample size varies with the instrument but a typical size is 8 mm by 8 mm with a typical height of 1 mm. Solid samples present a problem for AFM since the tip can shift the material as it scans the surface. Solutions or dispersions are best for applying as uniform of a layer of material as possible in order to get the most accurate value of particles' heights. This is usually done by spin-coating the solution onto freshly cleaved mica which allows the particles to stick to the surface once it has dried.

8.2.5 Applications of AFM

AFM is particularly versatile in its applications since it can be used in ambient temperatures and many different environments. It can be used in many different areas to analyze different kinds of samples such as semiconductors, polymers, nanoparticles, biotechnology, and cells amongst others. The most common application of AFM is for morphological studies in order to attain an understanding of the topography of the sample. Since it is common for the material to be in solution, AFM can also give the user an idea of the ability of the material to be dispersed as well as the homogeneity of the particles within that dispersion. It also can provide a lot of information about the particles being studied such as particle size, surface area, electrical properties, and chemical composition. Certain tips are capable of determining the principal mechanical, magnetic, and electrical properties of the material. For example, in magnetic force microscopy (MFM) the probe has a magnetic coating that senses magnetic, electrostatic, and atomic interactions with the surface.

This type of scanning can be performed in static or dynamic mode and depicts the magnetic structure of the surface.

8.2.5.1 AFM of carbon nanotubes

Atomic force microscopy is usually used to study the topographical morphology of these materials. By measuring the thickness of the material it is possible to determine if bundling occurred and to what degree. Other dimensions of the sample can also be measured such as the length and width of the tubes or bundles. It is also possible to detect impurities, functional groups (Figure 8.12), or remaining catalyst by studying the images. Various methods of producing nanotubes have been found and each demonstrates a slightly different profile of homogeneity and purity. These impurities can be carbon coated metal, amorphous carbon, or other allotropes of carbon such as fullerenes and graphite. These facts can be utilized to compare the purity and homogeneity of the samples made from different processes, as well as monitor these characteristics as different steps or reactions are performed on the material. The distance between the tip and the surface has proven itself to be an important parameter in noncontact mode AFM and has shown that if the tip is moved past the threshold distance, approximately $30\text{ }\mu\text{m}$, it can move or damage the nanotubes. If this occurs, a useful characterization cannot be performed due to these distortions of the image.

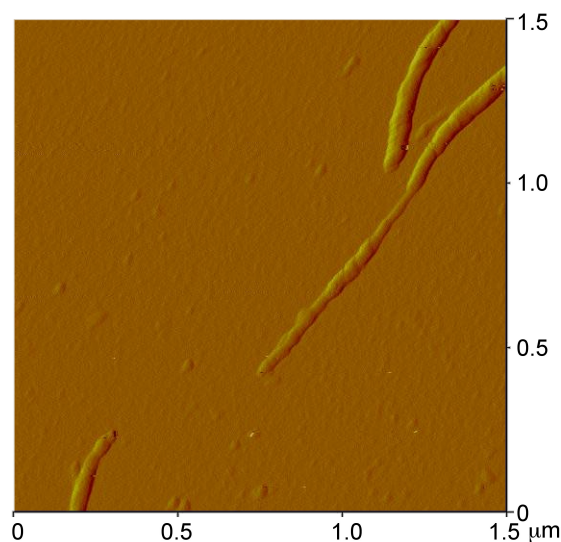


Figure 8.12: AFM image of a polyethyleneimine-functionalized single walled carbon nanotube (PEI-SWNT) showing the presence of PEI “globules” on the SWNT. Adapted from E. P. Dillon, C. A. Crouse, and A. R. Barron, *ACS Nano*, 2008, **2**, 156.

8.2.5.2 AFM of fullerenes

Atomic force microscopy is best applied to aggregates of fullerenes rather than individual ones. While the AFM can accurately perform height analysis of individual fullerene molecules, it has poor lateral resolution and it is difficult to accurately depict the width of an individual molecule. Another common issue that arises with contact AFM and fullerene deposited films is that the tip shifts clusters of fullerenes which can lead to discontinuities in sample images.

8.2.6 Bibliography

- R. Anderson and A. R. Barron, *J. Am. Chem. Soc.*, 2005, **127**, 10458.
- M. Bellucci, G. Gaggiotti, M. Marchetti, F. Micciulla, R. Mucciato, and M. Regi, *J. Physics: Conference Series*, 2007, **61**, 99.
- I. I. Bobrinetskii, V. N. Kukin, V. K. Nevolin, and M. M. Simunin. *Semiconductor*, 2008, **42**, 1496.
- S. H. Cohen and M. L. Lightbody. *Atomic Force Microscopy/Scanning Tunneling Microscopy 2*. Plenum, New York (1997).
- E. P. Dillon, C. A. Crouse, and A. R. Barron, *ACS Nano*, 2008, **2**, 156.
- C. Gu, C. Ray, S. Guo, and B. B. Akhremitchev, *J. Phys. Chem.*, 2007, **111**, 12898.
- G. Kaupp, *Atomic Force Microscopy, Scanning Nearfield Optical Microscopy and Nanoscratching: Application to Rough and Natural Surfaces*. Springer-Verlag, Berlin (2006).
- S. Morita, R. Wiesendanger, E. Meyer, and F. J. Giessibl. *Noncontact Atomic Force Microscopy*. Springer, Berlin (2002).

8.3 SEM and its Applications for Polymer Science ³

8.3.1 Introduction

The scanning electron microscope (SEM) is a very useful imaging technique that utilized a beam of electrons to acquire high magnification images of specimens. Very similar to the transmission electron microscope (TEM), the SEM maps the reflected electrons and allows imaging of thick ($\sim$ mm) samples, whereas the TEM requires extremely thin specimens for imaging; however, the SEM has lower magnifications. Although both SEM and TEM use an electron beam, the image is formed very differently and users should be aware of when each microscope is advantageous.

8.3.2 Microscopy physics

8.3.2.1 Image formation

All microscopes serve to enlarge the size of an object and allow people to view smaller regions within the sample. Microscopes form optical images and although instruments like the SEM have extremely high magnifications, the physics of the image formation are very basic. The simplest magnification lens can be seen in Figure 8.13. The formula for magnification is shown in (8.20), where M is magnification, f is focal length, u is the distance between object and lens, and v is distance from lens to the image.

$$M = \frac{f}{u - f} = \frac{v - f}{f} \quad (8.20)$$

³This content is available online at <<http://cnx.org/content/m38344/1.1/>>.

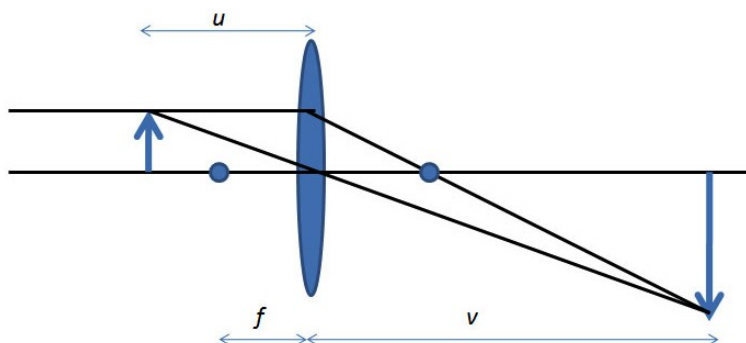


Figure 8.13: Basic microscope diagram illustrating inverted image and distances u , f , and v .

Multistage microscopes can amplify the magnification of the original object even more as shown in Figure 8.14. Where magnification is now calculated from (8.21), where f_1 , f_2 are focal distances with respect to the first and second lens and v_1 , v_2 are the distances from the lens to the magnified image of first and second lens, respectively.

$$M = \frac{(v_1 - f_1)(v_2 - f_2)}{f_1 f_2} \quad (8.21)$$

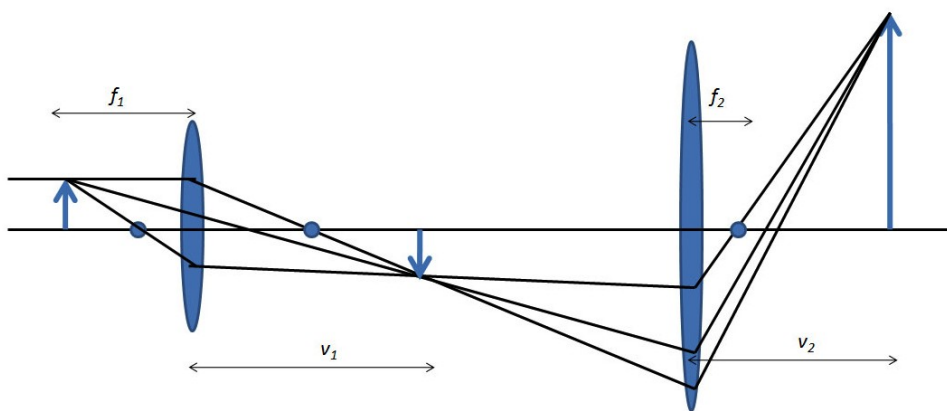


Figure 8.14: A schematic diagram of the optics used in a multistage microscope.

In reality, the objects we wish to magnify need to be illuminated. Whether or not the sample is thin enough to transmit light divides the microscope into two arenas. SEM is used for samples that do not

transmit light, whereas the TEM (transmission electron microscope) requires transparent samples. Due to the many frequencies of light from the introduced source, a condenser system is added to control the brightness and narrow the range of viewing to reduce aberrations, which distort the magnified image.

8.3.3 Electron microscopes

Microscope images can be formed instantaneous (as in the optical microscope or TEM) or by rastering (scanning) a beam across the sample and forming the image point-by-point. The latter is how SEM images are formed. It is important to understand the basic principles behind SEM that define properties and limitations of the image.

8.3.3.1 Resolution

The resolution of a microscope is defined as the smallest distance between two features that can be uniquely identified (also called resolving power). There are many limits to the maximum resolution of the SEM and other microscopes, such as imperfect lenses and diffraction effects. Each single beam of light, once passed through a lens, forms a series of cones called an *airy ring* (see Figure 8.15). For a given wavelength of light, the central spot size is inversely proportional to the aperture size (i.e., large aperture yields small spot size) and high resolution demands a small spot size.

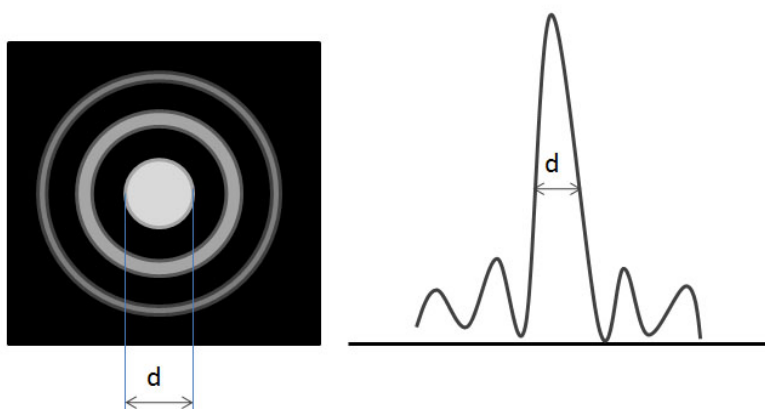


Figure 8.15: Airy ring illustrating center intensity (left) and intensity as a function of distance (right).

Aberrations distort the image and we try to minimize the effect as much as possible. Chromatic aberrations are caused by the multiple wavelengths present in *white* light. Spherical aberrations are formed by focusing inside and outside the ideal focal length and caused by the imperfections within the objective lenses. Astigmatism is because of further distortions in the lens. All aberrations decrease the overall resolution of the microscope.

8.3.3.2 Electrons

Electrons are charged particles and can interact with air molecules therefore the SEM and TEM instruments require extremely high vacuum to obtain images (10^{-7} atm). High vacuum ensures that very few air molecules are in the electron beam column. If the electron beam interacts with an air molecule, the air will become

ionized and damage the beam filament, which is very costly to repair. The charge of the electron allows scanning and also inherently has a very small deflection angle off the source of the beam.

The electrons are generated with a thermionic filament. A tungsten (W) or LaB_6 filament is chosen based on the needs of the user. LaB_6 is much more expensive and tungsten filaments meet the needs of the average user. The microscope can be operated as field emission (tungsten filament).

8.3.3.3 Electron scattering

To accurately interpret electron microscopy images, the user must be familiar with how high energy electrons can interact with the sample and how these interactions affect the image. The probability that a particular electron will be scattered in a certain way is either described by the cross section, σ , or mean free path, λ , which is the average distance which an electron travels before being scattered.

8.3.3.3.1 Elastic scatter

Elastic scatter, or Rutherford scattering, is defined as a process which deflects an electron but does not decrease its energy. The wavelength of the scattered electron can be detected and is proportional to the atomic number. Elastically scattered electrons have significantly more energy than other types and provide mass contrast imaging. The mean free path, λ , is larger for smaller atoms meaning that the electron travels farther.

8.3.3.3.2 Inelastic scatter

Any process that causes the incoming electron to lose a detectable amount of energy is considered inelastic scattering. The two most common types of inelastic scatter are phonon scattering and plasmon scattering. Phonon scattering occurs when a primary electron loses energy by exciting a phonon, atomic vibrations in a solid, and heats the sample a small amount. A Plasmon is an oscillation within the bulk electrons in the conduction band for metals. Plasmon scattering occurs when an electron interacts with the sample and produces plasmons, which typically have 5 - 30 eV energy loss and small λ .

8.3.3.3.3 Secondary effects

A secondary effect is a term describing any event which may be detected *outside* the specimen and is essentially how images are formed. To form an image, the electron must interact with the sample in one of the aforementioned ways and *escape* from the sample and be detected. *Secondary electrons* (SE) are the most common electrons used for imaging due to high abundance and are defined, rather arbitrarily, as electrons with less than 50 eV energy after exiting the sample. *Backscattered electrons* (BSE) leave the sample quickly and retain a high amount of energy; however there is a much lower yield of BSE. Backscattered electrons are used in many different imaging modes. Refer to Figure 8.16 for a diagram of interaction depths corresponding to various electron interactions.

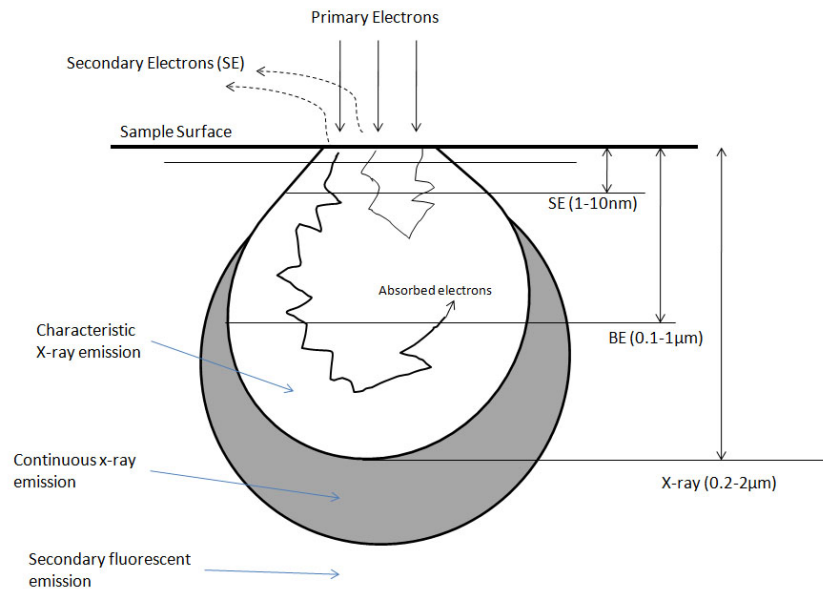


Figure 8.16: Diagram illustrating the depths at which various sample interactions occur.

8.3.4 SEM Construction

The SEM is made of several main components: electron gun, condenser lens, scan coils, detectors, specimen, and lenses (see Figure 8.17). Today, portable SEMs are available but the typical size is about 6 feet tall and contains the microscope column and the control console.

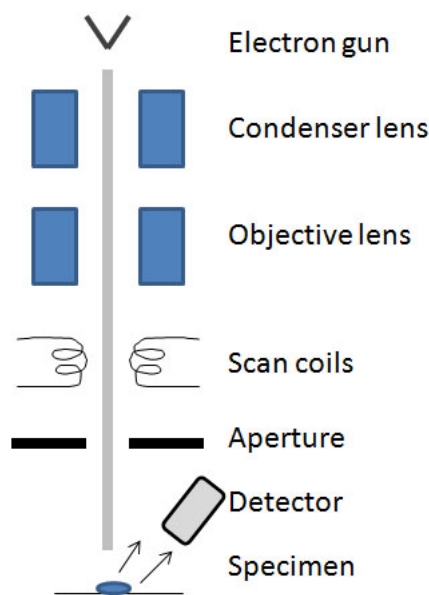


Figure 8.17: Schematic drawing of the SEM illustrating placement of electron generation, collimation process, sample interaction and electron detection.

A special feature of the SEM and TEM is known as *depth of focus*, dv/du the range of positions (depths) at which the image can be viewed with good focus, see (8.22). This allows the user to see more than a singular plane of a specified height in focus and essentially allows a range of three dimensional imaging.

$$\frac{dv}{du} = \frac{-v^2}{u^2} = -M^2 \quad (8.22)$$

8.3.4.1 Electron detectors (image formation)

The secondary electron detector (SED) is the main source of SEM images since a large majority of the electrons emitted from the sample are less than 50 eV. These electrons form textural images but cannot determine composition. The SEM may also be equipped with a backscatter electron detector (BSED) which collects the higher energy BSE's. Backscattered electrons are very sensitive to atomic number and can determine qualitative information about nuclei present (i.e., how much Fe is in the sample). Topographic images are taken by tilting the specimen 20 - 40° toward the detector. With the sample tilted, electrons are more likely to scatter off the top of the sample rather than interact within it, thus yielding information about the surface.

8.3.5 Sample preparation

The most effective SEM sample will be at least as thick as the interaction volume; depending on the image technique you are using (typically at least 2 μm). For the best contrast, the sample must be conductive or

the sample can be sputter-coated with a metal (such as Au, Pt, W, and Ti). Metals and other materials that are naturally conductive do not need to be coated and need very little sample preparation.

8.3.6 SEM of polymers

As previously discussed, to view features that are smaller than the wavelength of light, an electron microscope must be used. The electron beam requires extremely high vacuum to protect the filament and electrons must be able to adequately interact with the sample. Polymers are typically long chains of repeating units composed primarily of “lighter” (low atomic number) elements such as carbon, hydrogen, nitrogen, and oxygen. These lighter elements have fewer interactions with the electron beam which yields poor contrast, so often times a stain or coating is required to view polymer samples. SEM imaging requires a conductive surface, so a large majority of polymer samples are sputter coated with metals, such as gold.

The decision to view a polymer sample with an SEM (versus a TEM for example) should be evaluated based on the feature size you expect the sample to have. Generally, if you expect the polymer sample to have features, or even individual molecules, over 100 nm in size you can safely choose SEM to view your sample. For much smaller features, the TEM may yield better results, but requires much different sample preparation than will be described here.

8.3.6.1 Polymer sample preparation techniques

8.3.6.1.1 Sputter coating

A sputter coater may be purchased that deposits single layers of gold, gold-palladium, tungsten, chromium, platinum, titanium, or other metals in a very controlled thickness pattern. It is possible, and desirable, to coat only a few nm's of metal onto the sample surface.

8.3.6.1.2 Spin coating

Many polymer films are depositing via a spin coater which spins a substrate (often ITO glass) and drops of polymer liquid are dispersed an even thickness on top of the substrate.

8.3.6.1.3 Staining

Another option for polymer sample preparation is staining the sample. Stains act in different ways, but typical stains for polymers are osmium tetroxide (OsO_4), ruthenium tetroxide (RuO_4) phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$), hydrazine (N_2H_4), and silver sulfide (Ag_2S).

8.3.7 Examples

8.3.7.1 Comb-block copolymer (microstructure of cast film)

- Cast polymer film (see Figure 8.18).
- To view interior structure, the film was cut with a microtome or razor blade after the film was frozen in liquid N_2 and fractured.
- Stained with RuO_4 vapor (after cutting).
- Structure measurements were averaged over a minimum of 25 measurements.

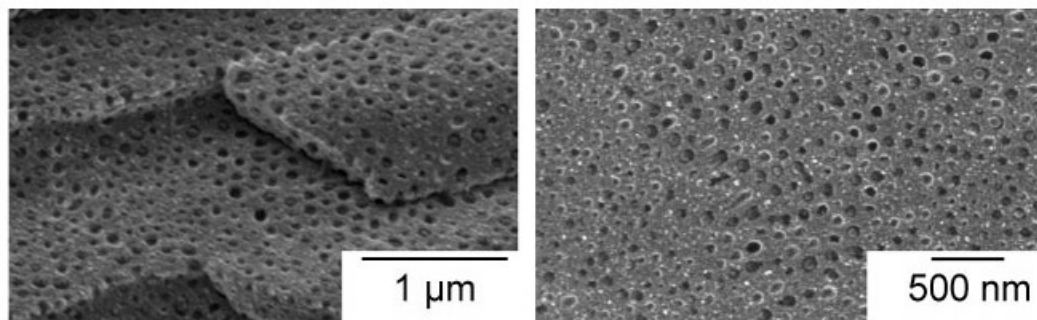


Figure 8.18: SEM micrograph of comb block copolymer showing spherical morphology and long range order. Adapted from M. B. Runge and N. B. Bowden, *J. Am. Chem. Soc.*, 2007, **129**, 10551. Copyright: American Chemical Society (2007).

8.3.7.1.1 Polystyrene-poly lactide bottlebrush copolymers (lamellar spacing)

- Pressed polymer samples into disks and annealed for 16 h at 170 °C.
- To determine ordered morphologies, the disk was fractured (see Figure 8.19).
- Used SEM to verify lamellar spacing from USAXS.

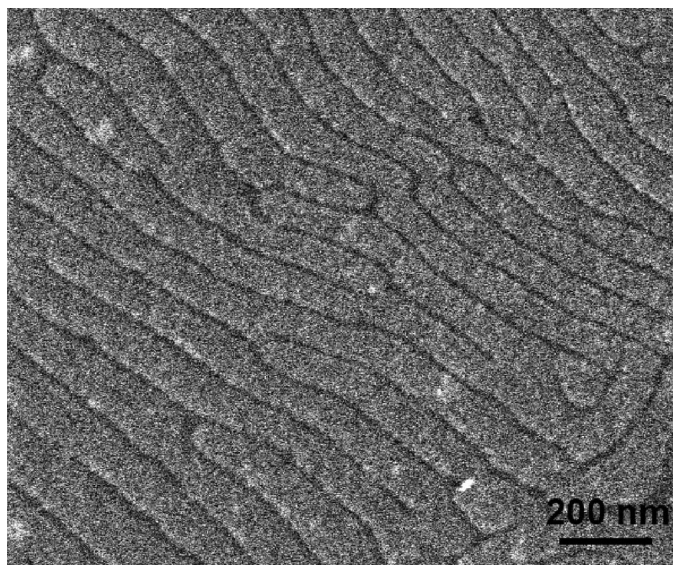


Figure 8.19: SEM image of a fractured piece of polymer SL-1. Adapted from J. Rzaev, *Macromolecules*, 2009, **42**, 2135. Copyright: American Chemical Society (2009).

8.3.7.1.2 SWNTs in ultrahigh molecular weight polyethylene

- Dispersed SWNTs in interactive polymer.
- Samples were sputter-coated in gold to enhance contrast.
- The films were solution-crystallized and the cross-section was imaged.
- Environmental SEM (ESEM) was used to show morphologies of composite materials.
- WD = 7 mm.
- Study was conducted to image sample before and after drawing of film.
- Images confirmed the uniform distribution of SWNT in PE (Figure 8.20).
- $M_W = 10,000$ Dalton.
- Study performed to compare transparency before and after UV irradiation.

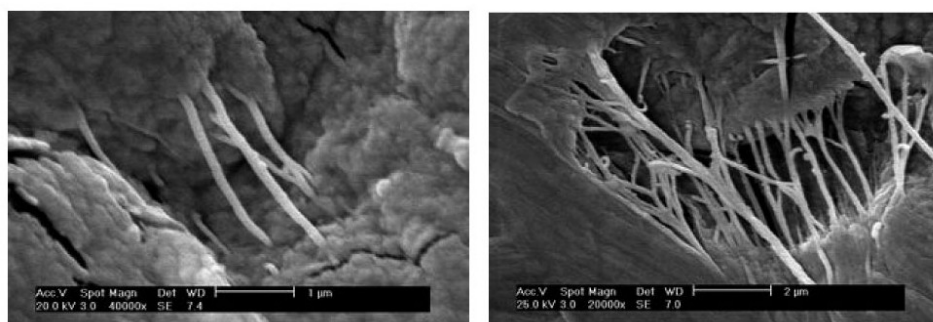


Figure 8.20: SEM images of crystallized SWNT-UHMWPE films before (left) and after (right) drawing at 120 °C. Adapted from Q. Zhang, D. R. Lippits, and S. Rastogi, *Macromolecules*, 2006, **39**, 658. Copyright: American Chemical Society (2006).

8.3.7.1.3 Nanostructures in conjugated polymers (nanoporous films)

- Polymer and NP were processed into thin films and heated to crosslink.
- SEM was used to characterize morphology and crystalline structure (Figure 8.21).
- SEM was used to determine porosity and pore size.
- Magnified orders of 200 nm - 1 μ m.
- WD = 8 mm.
- $M_W = 23,000$ Daltons
- Sample prep: spin coating a solution of poly-(thiophene ester) with copper NPs suspended on to ITO coated glass slides. Ziess, Supra 35

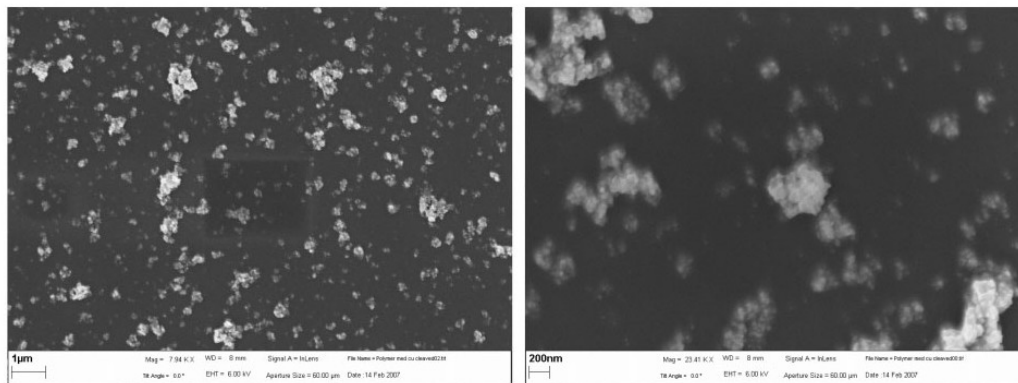


Figure 8.21: SEM images of thermocleaved film loaded with nanoparticles with scale bar 1 μm . Adapted from J. W. Andreasen, M. Jorgensen, and F. C. Krebs, *Macromolecules*, 2007, **40**, 7758. Copyright: American Chemical Society (2007).

8.3.7.1.4 Cryo-SEM colloid polystyrene latex particles (fracture patterns)

- Used cryogenic SEM (cryo-SEM) to visualize the microstructure of particles (Figure 8.22).
- Particles were immobilized by fast-freezing in liquid N_2 at -196°C .
- Sample is fractured (-196°C) to expose cross section.
- 3 nm sputter coated with platinum.
- Shapes of the nanoparticles after fracture were evaluated as a function of crosslink density.

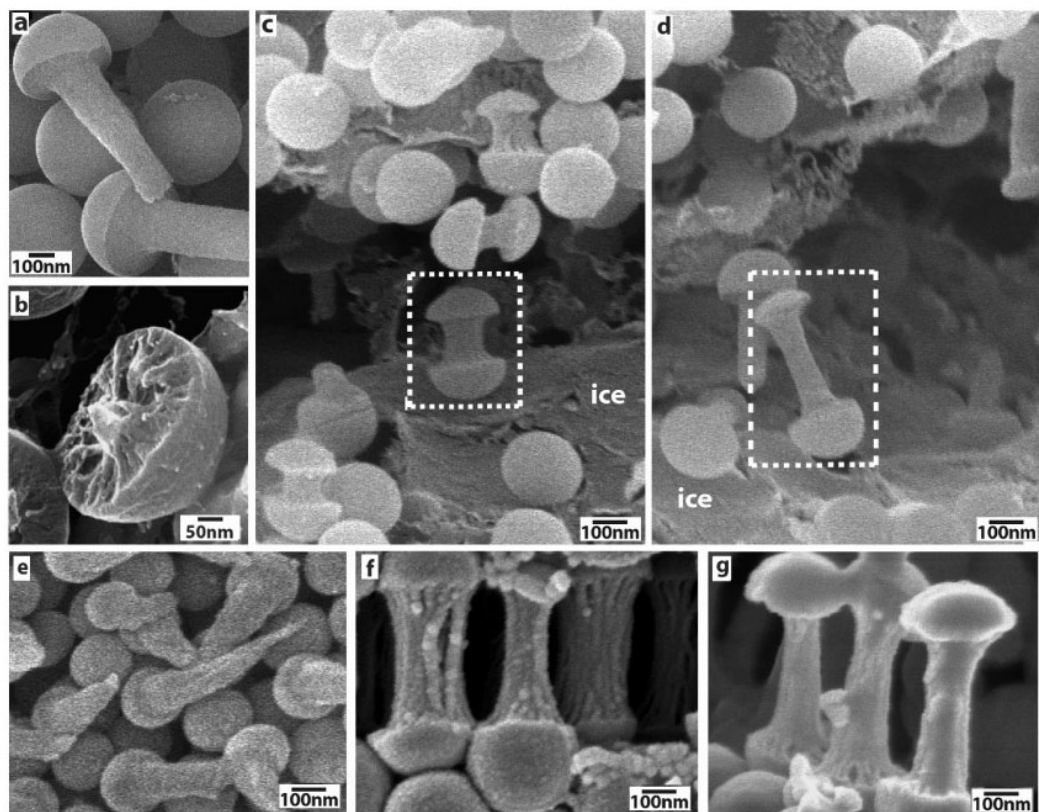


Figure 8.22: Cryo-SEM images of plastically drawn polystyrene and latex particles. Adapted from H. Ge, C. L. Zhao, S. Porzio, L. Zhuo, H. T. Davis, and L. E. Scriven, *Macromolecules*, 2006, **39**, 5531. Copyright: American Chemical Society (2006).

8.3.8 Bibliography

- H. Ge, C. L. Zhao, S. Porzio, L. Zhuo, H. T. Davis, and L. E. Scriven, *Macromolecules*, 2006, **39**, 5531.
- J. Rzaev, *Macromolecules*, 2009, **42**, 2135.
- J. W. Andreasen, M. Jorgensen, and F. C. Krebs, *Macromolecules*, 2007, **40**, 7758.
- M. B. Runge and N. B. Bowden, *J. Am. Chem. Soc.*, 2007, **129**, 10551.
- P. J. Goodhew, J. Humphreys, and R. Beanland, *Electron Microscopy and Analysis*, Taylor & Francis Inc., New York (2001).
- Q. Zhang, D. R. Lippits, and S. Rastogi, *Macromolecules*, 2006, **39**, 658.

8.4 Catalyst Characterization Using Thermal Conductivity Detector ⁴

8.4.1 Introduction

A catalyst is a "substance that accelerates the rate of chemical reactions without being consumed". Some reactions, such as the hydrodechlorination of TCE, (8.23), don't occur spontaneously, but can occur in the presence of a catalyst.



Metal dispersion is a common term within the catalyst industry. The term refers to the amount of metal that is active for a specific reaction. Let's assume a catalyst material has a composition of 1 wt% palladium and 99% alumina (Al_2O_3) (Figure 8.23). Even though the catalyst material has 1 wt% of palladium, not all the palladium is active. The material might be oxidized due to air exposure or some of the material is not exposed to the surface (Figure 8.24), hence it can't participate in the reaction. For this reason it is important to characterize the material.



Figure 8.23: A photograph of a sample of commercially available 1 wt% Pd/ Al_2O_3 .

⁴This content is available online at <<http://cnx.org/content/m43579/1.1/>>.

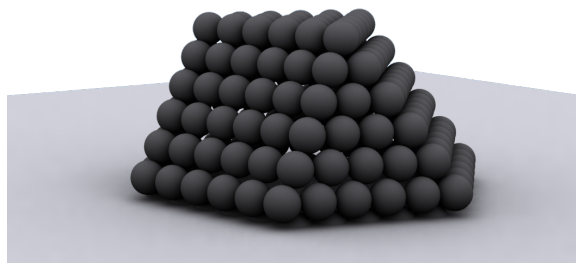


Figure 8.24: Representation of Pd nanoparticles on Al_2O_3 . Some palladium atoms are exposed to the surface, while some other lay below the surface atoms and are not accessible for reaction.

In order for Pd to react according to (8.23), it needs to be in the metallic form. Any oxidized palladium will be inactive. Thus, it is important to determine the oxidation state of the Pd atoms on the surface of the material. This can be accomplished using an experiment called temperature programmed reduction (TPR). Subsequently, the percentage of active palladium can be determined by hydrogen chemisorption. The percentage of active metal is an important parameter when comparing the performance of multiple catalyst. Usually the rate of reaction is normalized by the amount of active catalyst.

8.4.2 Principles of thermal conductivity

Thermal conductivity is the ability of a chemical specie to conduct heat. Each gas has a different thermal conductivity. The units of thermal conductivity in the international system of units are $\text{W/m}\cdot\text{K}$. Table 8.2, shows the thermal conductivity of some common gasses.

Gas	Thermal conductivity ($\text{W/m}\cdot\text{K}$)
Hydrogen	0.18050
Argon	0.01772
Helium	0.15130
Carbon Monoxide	0.02614

Table 8.2: Thermal conductivity values for common gasses.

8.4.3 Thermal conductivity detector

A thermal conductivity detector has four filaments that change resistance according to the thermal conductivity of the gas flowing over it. Two filaments measure the reference gas and the other two measures the sample gas. The detector is isothermal; it will increase or decrease the voltage in each of the resistors in order to maintain a constant temperature. The temperature of the detector is 125°C . When both the reference and samples gas have the same composition and same flow rate, the resistors are balanced and the detector will zero the signal. If there is a change in flow rate or in the gas composition the detector will react

to maintain the constant temperature. The detector circuitry can be described using a Wheatstone bridge configuration as shown in Figure 8.25. If the gas flowing through the sample has a higher thermal conductivity the filament will cool down, the detector will apply a higher voltage to keep a constant temperature and this will be recorded as a positive signal.

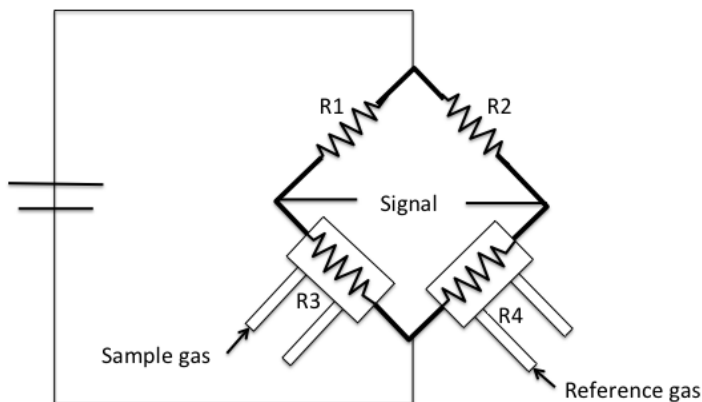


Figure 8.25: A simplified circuit diagram of a thermal conductivity detector.

This detector is part of a typical commercial instrument such as a Micromeritics AutoChem 2920 (Figure 8.26). This instrument is an automated analyzer with the ability to perform chemical adsorption and temperature-programmed reactions on a catalyst, catalyst support, or other materials.



Figure 8.26: A photograph of a Micromeritics AutoChem 2920.

8.4.4 Temperature programmed reduction (TPR)

TPR will determine the number of reducible species on a catalyst and will tell at what temperature each of these species was reduced. For example palladium is ordinarily found as Pd(0) or Pd(II), i.e., oxidation states 0 and +2. Pd(II) can be reduced at very low temperatures (5 - 10 °C) to Pd(0) following (8.24).



A 128.9 mg 1wt% Pd/Al₂O₃ samples is used for the experiment, Figure 8.27. Since we want to study the oxidation state of the commercial catalyst, no pre-treatment needs to be executed to the sample. A 10% hydrogen-argon mixture is used as analysis and reference gas. Argon has a low thermal conductivity and hydrogen has a much higher thermal conductivity. All gases will flow at 50 cm³/min. The TPR experiment will start at an initial temperature of 200 K, temperature ramp 10 K/min, and final temperature of 400 K. The H₂/Ar mixture is flowed through the sample, and past the detector in the analysis port. While in the reference port the mixture doesn't become in contact with the sample. When the analysis gas starts flowing over the sample, a baseline reading is established by the detector. The baseline is established at the initial temperature to ensure there is no reduction. While this gas is flowing, the temperature of the sample is increased linearly with time and the consumption of hydrogen is recorded. Hydrogen atoms react with oxygen atoms to form H₂O.

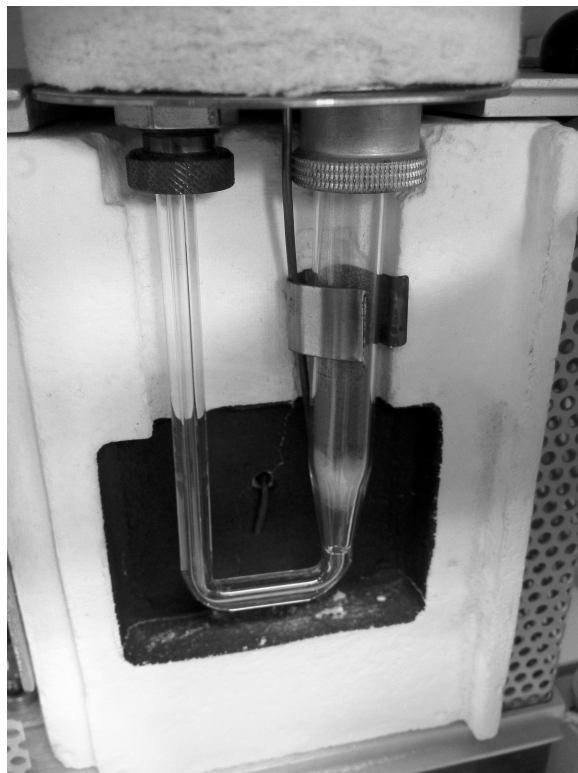


Figure 8.27: A sample of Pd/Al₂O₃ in a typical sample holder.

Water molecules are removed from the gas stream using a cold trap. As a result, the amount of hydrogen in the argon/hydrogen gas mixture decreases and the thermal conductivity of the mixture also decrease. The change is compared to the reference gas and yields to a hydrogen uptake volume. Figure 8.28 is a typical TPR profile for PdO.

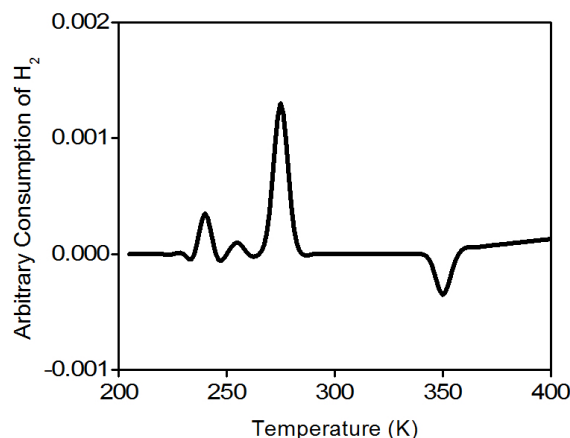


Figure 8.28: A typical TPR profile of PdO. Adapted from R. Zhang, J. A. Schwarz, A. Datye, and J. P. Baltrus, *J. Catal.*, 1992, **138**, 55.

8.4.5 Pulse chemisorption

Once the catalyst (1 wt% Pd/Al₂O₃) has been completely reduced, the user will be able to determine how much palladium is active. A pulse chemisorption experiment will determine active surface area, percentage of metal dispersion and particle size. Pulses of hydrogen will be introduced to the sample tube in order to interact with the sample. In each pulse hydrogen will undergo a dissociative adsorption on to palladium active sites until all palladium atoms have reacted. After all active sites have reacted, the hydrogen pulses emerge unchanged from the sample tube. The amount of hydrogen chemisorbed is calculated as the total amount of hydrogen injected minus the total amount eluted from the system.

8.4.6 Data collection for hydrogen pulse chemisorption

The sample from previous experiment (TPR) will be used for this experiment. Ultra high-purity argon will be used to purge the sample at a flow rate of 40 cm³/min. The sample will be heated to 200 °C in order to remove all chemisorbed hydrogen atoms from the Pd(0) surface. The sample is cooled down to 40 °C. Argon will be used as carrier gas at a flow of 40 cm³/min. Filaments temperature will be 175 °C and the detector temperature will be 110 °C. The injection loop has a volume of 0.03610 cm³ @ STP. As shown in Figure 8.29., hydrogen pulses will be injected in to the flow stream, carried by argon to become in contact and react with the sample. It should be noted that the first pulse of hydrogen was almost completely adsorbed by the sample. The second and third pulses show how the samples is been saturated. The positive value of the TCD detector is consistent with our assumptions. Since hydrogen has a higher thermal conductivity than argon, as it flows through the detector it will tend to cool down the filaments, the detector will then apply a positive voltage to the filaments in order to maintain a constant temperature.

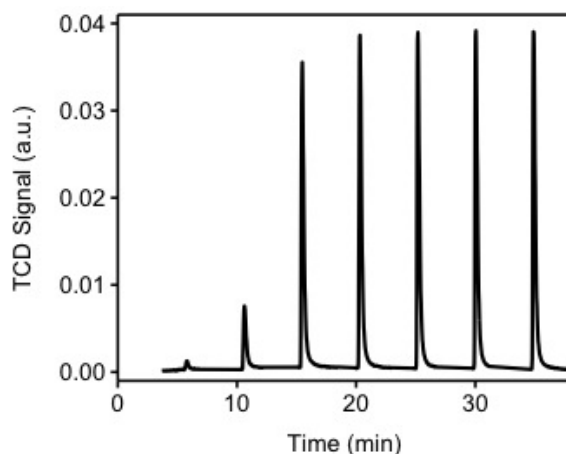


Figure 8.29: A typical hydrogen pulse chemisorption profile of 1 wt% Pd/Al₂O₃.

8.4.7 Pulse chemisorption data analysis

Table 8.3 shows the integration of the peaks from Figure 8.29. This integration is performed by an automated software provided with the instrument. It should be noted that the first pulse was completely consumed by the sample, the pulse was injected between time 0 and 5 minutes. From Figure 8.29 we observe that during the first four pulses, hydrogen is consumed by the sample. After the fourth pulse, it appears the sample is not consuming hydrogen. The experiment continues for a total of seven pulses, at this point the software determines that no consumption is occurring and stops the experiment. Pulse eight is denominated the "saturation peak", meaning the pulse at which no hydrogen was consumed.

Pulse n	Area
1	0
2	0.000471772
3	0.00247767
4	0.009846683
5	0.010348201
6	0.010030243
7	0.009967717
8	0.010580979

Table 8.3: Hydrogen pulse chemisorption data.

Using (8.25) the change in area (Δarea_n) is calculated for each peak pulse area (area_n) and compared to that of the saturation pulse area ($\text{area}_{\text{saturation}} = 0.010580979$). Each of these changes in area is proportional

to an amount of hydrogen consumed by the sample in each pulse. Table 8.4 Shows the calculated change in area.

$$\Delta\text{Area}_n = \text{Area}_{\text{saturation}} - \text{Area}_n \quad (8.25)$$

Pulse n	Area _n	ΔArea _n
1	0	0.010580979
2	0.000471772	0.0105338018
3	0.00247767	0.008103309
4	0.009846683	0.000734296
5	0.010348201	0.000232778
6	0.010030243	0.000550736
7	0.009967717	0.000613262
8	0.010580979	0

Table 8.4: Hydrogen pulse chemisorption data with ΔArea.

The Δarea_n values are then converted into hydrogen gas consumption using (8.26), where F_c is the area-to-volume conversion factor for hydrogen and SW is the weight of the sample. F_c is equal to 2.6465 cm³/peak area. Table 8.5 shows the results of the volume adsorbed and the cumulative volume adsorbed. Using the data on Table 8.5, a series of calculations can now be performed in order to have a better understanding of our catalyst properties.

$$V_{\text{adsorbed}} = \frac{\Delta\text{Area}_n \times F_c}{SW} \quad (8.26)$$

Pulse n	area _n	Δarea _n	V _{adsorbed} (cm ³ /g STP)	Cumulative quantity (cm ³ /g STP)
1	0	0.0105809790	0.2800256	0.2800256
2	0.000471772	0.0105338018	0.2787771	0.5588027
3	0.00247767	0.0081033090	0.2144541	0.7732567
4	0.009846683	0.0007342960	0.0194331	0.7926899
5	0.010348201	0.0002327780	0.0061605	0.7988504
6	0.010030243	0.0005507360	0.0145752	0.8134256
<i>continued on next page</i>				

7	0.009967717	0.0006132620	0.0162300	0.8296556
8	0.010580979	0	0.0000000	0.8296556

Table 8.5: Includes the volume adsorbed per pulse and the cumulative volume adsorbed.

8.4.7.1 Gram molecular weight

Gram molecular weight is the weighted average of the number of moles of each active metal in the catalyst. Since this is a monometallic catalyst, the gram molecular weight is equal to the molecular weight of palladium (106.42 [g/mol]). The GMW_{Calc} is calculated using (8.27), where F is the fraction of sample weight for metal N and $W_{\text{atomic}N}$ is the gram molecular weight of metal N (g/g-mole). (8.28) shows the calculation for this experiment.

$$\text{GMW}_{\text{Calc}} = \frac{1}{\left(\frac{F_1}{W_{\text{atomic}1}}\right) + \left(\frac{F_2}{W_{\text{atomic}2}}\right) + \dots + \left(\frac{F_N}{W_{\text{atomic}N}}\right)} \quad (8.27)$$

$$\text{GMW}_{\text{Calc}} = \frac{1}{\left(\frac{F_1}{W_{\text{atomicPd}}}\right)} = \frac{W_{\text{atomicPd}}}{F_1} = \frac{106.42 \frac{\text{g}}{\text{g-mole}}}{1} = 106.42 \frac{\text{g}}{\text{g-mole}} \quad (8.28)$$

8.4.7.2 Metal dispersion

The metal dispersion is calculated using (8.29), where PD is the percent metal dispersion, V_s is the volume adsorbed (cm^3 at STP), SF_{Calc} is the calculated stoichiometry factor (equal to 2 for a palladium-hydrogen system), SW is the sample weight and GMW_{Calc} is the calculated gram molecular weight of the sample [g/g-mole]. Therefore, in (8.30) we obtain a metal dispersion of 6.03%.

$$PD = 100 \times \left(\frac{V_s \times \text{SF}_{\text{Calc}}}{SW \times 22414} \right) \times \text{GMW}_{\text{Calc}} \quad (8.29)$$

$$PD = 100 \times \left(\frac{0.8296556 [\text{cm}^3] \times 2}{0.1289 [\text{g}] \times 22414 \left[\frac{\text{cm}^3}{\text{mol}} \right]} \right) \times 106.42 \left[\frac{\text{g}}{\text{g-mol}} \right] = 6.03\% \quad (8.30)$$

8.4.7.3 Metallic surface area per gram of metal

The metallic surface area per gram of metal is calculated using (8.31), where $\text{SA}_{\text{Metallic}}$ is the metallic surface area (m^2/g of metal), SW_{Metal} is the active metal weight, SF_{Calc} is the calculated stoichiometric factor and SA_{Pd} is the cross sectional area of one palladium atom (nm^2). Thus, in (8.30) we obtain a metallic surface area of $2420.99 \text{ m}^2/\text{g-metal}$.

$$\text{SA}_{\text{Metallic}} = \left(\frac{V_s}{SW_{\text{Metal}} \times 22414} \right) \times (\text{SF}_{\text{Calc}}) \times (6.022 \times 10^{23}) \times \text{SA}_{\text{Pd}} \quad (8.31)$$

$$\text{SA}_{\text{Metallic}} = \left(\frac{0.8296556 [\text{cm}^3]}{0.001289 [\text{g}_{\text{metal}}] \times 22414 \left[\frac{\text{cm}^3}{\text{mol}} \right]} \right) \times (2) \times (6.022 \times 10^{23} \left[\frac{\text{atoms}}{\text{mol}} \right]) \times 0.07 \left[\frac{\text{nm}^2}{\text{atom}} \right] = 2420.99 \left[\frac{\text{m}^2}{\text{g-metal}} \right] \quad (8.32)$$

8.4.7.4 Active particle size

The active particle size is estimated using (8.33), where D_{Calc} is palladium metal density (g/cm^3), SW_{Metal} is the active metal weight, GMW_{Calc} is the calculated gram molecular weight ($\text{g}/\text{g-mole}$), and SA_{Pd} is the cross sectional area of one palladium atom (nm^2). As seen in (8.34) we obtain an optical particle size of 2.88 nm.

$$APS = \frac{6}{D_{\text{Calc}} \times \left(\frac{W_s}{GMW_{\text{Calc}}} \right) \times (6.022 \times 10^{23}) \times SA_{\text{Metallic}}} \quad (8.33)$$

$$APS = \frac{600}{(1.202 \times 10^{-20} \left[\frac{\text{g}_{\text{Pd}}}{\text{nm}^3} \right]) \times \left(\frac{0.001289 [\text{g}]}{106.42 \left[\frac{\text{g}_{\text{Pd}}}{\text{mol}} \right]} \right) \times (6.022 \times 10^{23} \left[\frac{\text{atoms}}{\text{mol}} \right]) \times \left(2420.99 \left[\frac{\text{m}^2}{\text{g}_{\text{Pd}}} \right] \right)} = 2.88 \text{ nm} \quad (8.34)$$

In a commercial instrument, a summary report will be provided which summarizes the properties of our catalytic material. All the equations used during this example were extracted from the AutoChem 2920-User's Manual.

Properties	Value
Palladium atomic weight	106.4 g/mol
Atomic cross-sectional area	0.0787 nm ²
Metal density	12.02 g/cm ³
Palladium loading	1 wt%
Metal dispersion	6.03%
Metallic surface area	2420.99 m ² /g-metal
Active particle diameter (hemisphere)	2.88 nm

Table 8.6: Summary report provided by Micromeritics AuthoChem 2920.

8.4.8 References

- A. J. Canty, *Accounts Chem. Res.*, 1992, **25**, 83.
- H. S. Fogler, *Elements of Chemical Reaction Engineering*, Prentice-Hall, New York (1992).
- Micromeritics Instrument Corporation, *AutoChem 2920 – Automated catalyst characterization system – Operators Manual*, V4.01 (2009).
- M. O. Nutt, K. N. Heck, P. Alvarez, and M. S. Wong, *Appl. Catal. B-Environ.*, 2006, **69**, 115.
- M. O. Nutt, J. B. Hughes, and M. S. Wong, *Environ. Sci. Technol.*, 2005, **39**, 1346.
- P. A. Webb and C. Orr, *Analytical Methods in Fine Particle Technology*, Micromeritics Instrument Corp, 1997.
- R. Zhang, J. A. Schwarz, A. Datye, and J. P. Baltrus, *J. Catal.*, 1992, **138**, 55.

Chapter 9

Device Performance

9.1 A Simple Test Apparatus to Verify the Photoresponse of Experimental Photovoltaic Materials and Prototype Solar Cells ¹

9.1.1 Introduction

One of the problems associated with testing a new unproven photovoltaic material or cell design is that significant processing required in order to create a fully functioning solar cell. If it is desired to screen a wide range of materials or synthetic conditions it can be time consuming (and costly of research funds) to prepare fully functioning devices. In addition, the success of each individual cell may be more dependent on fabrication steps not associated with the variations under study. For example, lithography and metallization could cause more variability than the parameters of the materials synthesis. Thus, the result could be to give no useful information as to the viability of each material under study, or even worse a false indication of research direction.

So-called *quick and dirty* qualitative measurements can be employed to assess not only the relative photoresponse of new absorber layer materials, but also the relative power output of photovoltaic devices. The measurement procedure can provide a simple, inexpensive and rapid evaluation of cell materials and structures that can help guide the development of new materials for solar cell applications.

9.1.2 Equipment needs

Everything needed for the measurements can be purchased at a local electronics store and a hardware or big box store. Needed items are:

- Two handheld digital voltmeter with at least ± 0.01 mV sensitivity (0.001 mV is better, of course).
- A simple breadboard and associated wiring kit.
- A selection of standard size and wattage resistors ($1/8$ - 1 Watt, 1 - 1000 ohms).
- A selection of wire wound potentiometers (0 - 10 ohms; 0 - 100 ohms; 0 - 1000 ohms) if I-V tracing is desired.
- A light source. This can be anything from a simple flood light to an old slide projector.
- A small fan or other cooling device for “steady state” (i.e., for measurements that last more than a few seconds such as tracing an I-V curve).
- 9 volt battery and holder or simple ac/dc low voltage power supply.

¹This content is available online at <<http://cnx.org/content/m42271/1.1/>>.

9.1.3 Measurement of the photo-response of an experimental solar cell

A qualitative measurement of a solar cell's current-voltage (I-V) characteristics can be obtained using the simple circuit diagram illustrated in Figure 9.1. Figure 9.2 shows an I-V test setup using a household flood lamp for the light source. A small fan sits to the right just out of the picture.

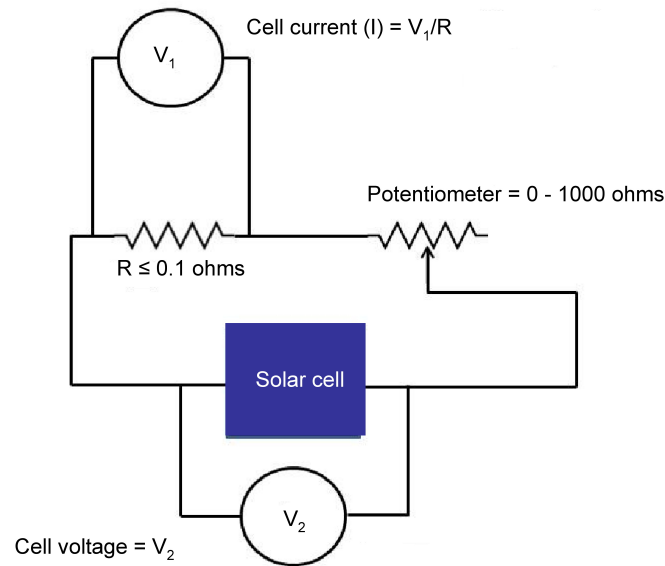


Figure 9.1: Simple circuit diagram for I-V measurement of a prototype solar cell.



Figure 9.2: Simple test apparatus for qualitative measurement of the current-voltage output from an experimental thin film solar cell.

Driving the potentiometer to its maximum value will place the cell close to open circuit operation, depending on the potentiometer range, so that the open circuit voltage can be simply extrapolated from the I versus V curve. If desired, the circuit can simply be opened to make the actual measurement once the rest of the data have been recorded. Data in this case were simply recorded by hand and later entered into a spreadsheet so an I - V plot could be generated. A sample plot is shown in Figure 9.3. Keep in mind that cell efficiency cannot be determined with this technique unless the light source has been calibrated and color corrected to match terrestrial sunlight. The fact that the experimental device actually generated net power was the result sought. The shape of the curve and the very low voltage are the result of very large resistive losses in the device along with a very “leaky” junction.

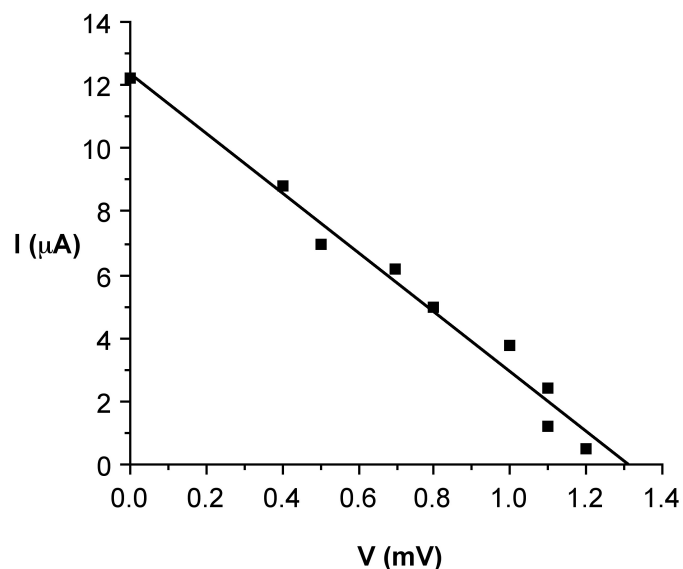


Figure 9.3: A sample plot of I-V data taken with test setup shown in Figure 9.1 and Figure 9.2.

One improvement that can be made to the above system is to replace the floodlight with a simple slide projector. The floodlight will typically have a spectrum very heavily weighted in the red and infrared and will be deficient in the shorter wavelengths. Though still not a perfect match to the solar spectrum, the slide projector does at least have more output at the shorter wavelengths; at the same time it will have less IR output compared to the floodlight and the combination should give a somewhat more representative response. A typical set up is shown in Figure 9.4.



Figure 9.4: Test setup using a slide projector.

The mirror in Figure 9.4 serves two purposes. First, it turns the beam so the test object can be laid flat a measurement bed and second it serves to collimate and concentrate the beam by focusing it on a smaller area, giving a better approximation of terrestrial solar intensity over a range of intensities such as AM2 (air mass 2) through AM0 (Figure 9.5). An estimate of the intensity can be made using a calibrated silicon solar cell of the sort that can be purchased online from any of several scientific hobby shops such as Edmunds Scientific. While still far from enabling a quantitative measurement of device output, the technique will at least provide indications within a ballpark range of actual cell efficiency.

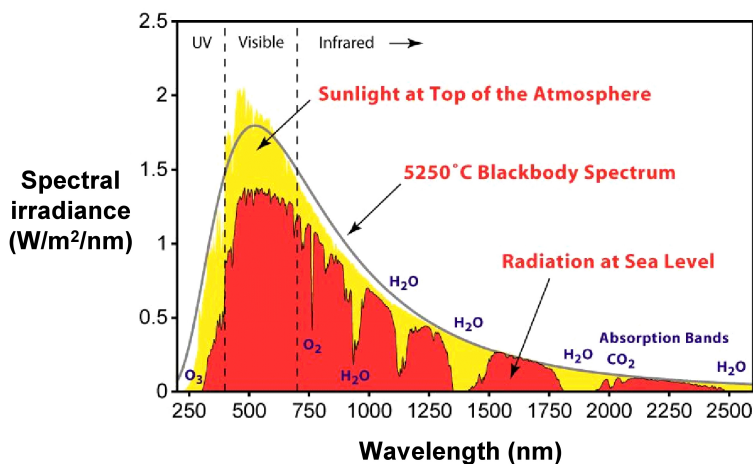


Figure 9.5: Solar irradiance spectrum at AM 0 (yellow) and AM2 (red). Adapted from M. Pagliaro, G. Palmisano, and R. Ciriminna, *Flexible Solar Cells*, John Wiley, New York (2008).

Figure 9.6 shows a measurement made with the test device placed at a distance from the mirror for which the intensity was previously determined to be equivalent to AM1 solar intensity, or 1000 watts per square meter. Since the beam passes through the projector lens and reflects from the second surface of the slightly concave mirror, there is essentially no UV light left in the beam that could be harmful to the naked eye. Still, if this technique is used, it is recommended that observations be made through a piece of ordinary glass such as eyeglasses or even a small glass shield inserted for that purpose. The blue area in the figure represents the largest rectangle that can be drawn under the curve and gives the maximum output power of the cell, which is simply the product of the current and voltage at maximum power.

NOTE: Figure 9.3 is a plot of current density, obtained by dividing the current from the device by its area. It is common to normalize the output in this manner.

If the power density of the incident light (P_0) is known in W/cm^2 , the device efficiency can be obtained by dividing the maximum power (as determined from I_m and V_m) by the incident power density times the area of the cell (A_{cell}), (9.1).

$$\eta = I_m V_m / P_0 A_{\text{cell}} \quad (9.1)$$



Figure 9.6: The picture shows the relative brightness of the light beam at an approximate intensity of 1000 W/m^2 . A small concave mirror serves to both turn the beam and to concentrate it a small amount to reach that level.

9.1.4 Measurement of the photoconductivity of experimental photovoltaic materials

In many cases it is beneficial to determine the photoconductivity of a new material prior to cell fabrication. This allows for the rapid screening of materials or synthesis variable of a single material even before issues of cell design and construction are considered.

Figure 9.7 shows the circuit diagram of a simple photoconductivity test made with a slightly different set up compared to that shown above. In this case a voltage is placed across the sample after it has been connected to a resistor placed in series with the sample. A simple 9 V battery secured with a battery holder or a small ac to dc power converter can be used to supply the voltage. The sample and resistor sit inside a small box with an open top.

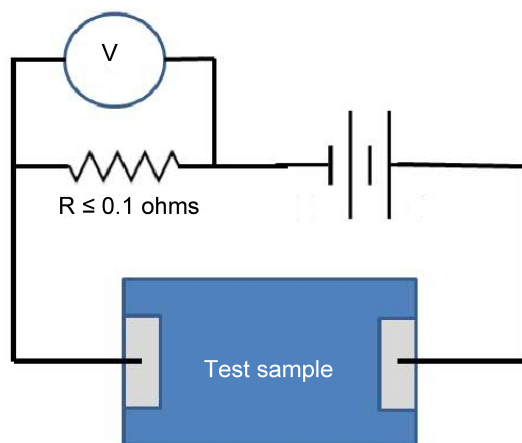


Figure 9.7: Circuit diagram for simple photoconductance test.

The voltage across (in this case) the 10 ohm resistor was measured with a shutter held over the sample (a simple piece of cardboard sitting on the top of the box) and with the shutter removed. The difference in voltage is a direct indication of the change in the photoconductance of the sample and again is a very quick and simple test to see if the material being developed does indeed have a photoresponse of some sort without having to make a full device structure. Adjusting the position of the light source so that the incident light power density at the sample surface is 200 or 500 or 1000 W/m^2 enables an approximate numerical estimate of the photocurrent that was generated and again can help guide the development of new materials for solar cell applications. The results from such a measurement are shown in Figure 9.8 for a sample of carbon nanotubes (CNT) coated with CdSe by liquid phase deposition (LPD).

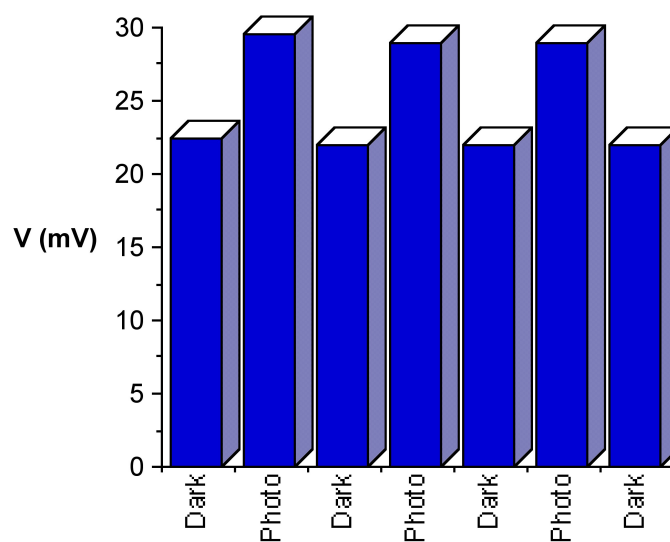


Figure 9.8: Photoresponse of a carbon nanotube (CNT) carpet coated with CdSe by liquid phase deposited.

Index of Keywords and Terms

Keywords are listed by the section with that keyword (page numbers are in parentheses). Keywords do not necessarily appear in the text of the page. They are merely associated with that section. *Ex.* apples, § 1.1 (1) **Terms** are referenced by the page they appear on. *Ex.* apples, 1

- 1** 12-16, § 7.4.2(580), § 7.4.4(599)
- A** AAS, § 1.1(3)
 aberration, § 8.3(639)
 absorbance, § 3.3.3(276), § 3.4.1(288), § 7.4.3(588)
 absorber, § 9.1(661)
 absorption, § 1.1(3), § 1.6(47), § 3.3.4(283), § 3.5.1(295), § 4.3(413), § 6.6(509)
 acac, § 2.5.3(172)
 acetone, § 3.4.1(288)
 acetylacetonate, § 2.5.3(172)
 acid, § 3.7.4(336)
 ACQ, § 3.5.1(295)
 activity, § 1.5(43)
 addition, § 1.1(3)
 adsorption, § 2.7(185)
 adsorption, § 6.5.1(502)
 aerosol, § 6.7(518)
 AES, § 1.9(84)
 AFM, § 5.2(429), § 7.3.1(560), § 7.6(619), § 8.1(623), § 8.2(634)
 AFS, § 1.7.2(60)
 AgCl, § 1.5(43)
 AIE, § 3.5.1(295)
 air, § 7.3.1(560)
 Airy disk, § 7.1(535)
 airy ring, § 8.3(639)
 alcohol, § 3.7.1(321)
 alkane, § 3.3.2(275)
 alkene, § 3.3.2(275), § 3.7.1(321)
 alkyl, § 3.7.1(321)
 alkyne, § 3.3.2(275), § 3.7.1(321)
 alloy, § 6.2(459)
 alpha, § 1.13(111)
 alumina, § 8.4(650)
 aluminum, § 1.10(90), § 6.1(441), § 6.2(459)
 AM0, § 9.1(661)
 AM1, § 9.1(661)
 AM2, § 9.1(661)
 amalgamation, § 1.7.2(60)
 amine, § 2.5.2(160), § 6.3.2(479)
 amino acid, § 6.6(509)
 analysis, § 1.1(3), § 1.2(17), § 1.3(24), § 1.4(28), § 1.8.1(75), § 1.8.2(80), § 1.9(84), § 1.10(90), § 2.1(119), § 3.9.1(365), § 6.5.1(502), § 6.6(509)
 analyte, § 1.2(17), § 4.1(397)
 analytical, § 6.7(518)
 analytical chemistry, § 3.10(380)
 analyzer, § 1.9(84)
 anion, § 6.3.2(479)
 anisotropic, § 3.8.2(359)
 anisotropy, § 3.7.5(340)
 anti-Stokes, § 3.2.1(241)
 antimony, § 6.2(459)
 antisite, § 6.1(441)
 aperture, § 8.3(639)
 apparatus, § 2.1(119), § 9.1(661)
 application, § 1.9(84)
 aqueous, § 4.2(408)
 aqueous synthesis, § 3.6.2(317)
 Ar, § 4.3(413)
 area, § 2.7(185), § 8.4(650)
 argon, § 1.7.3(61), § 2.5.3(172), § 2.8(196), § 4.3(413), § 8.4(650)
 aromatic, § 3.7.1(321)
 Arrhenius, § 4.3(413)
 arsenic, § 1.3(24), § 6.5.1(502)
 arsenide, § 6.1(441), § 6.2(459)
 asymmetric, § 3.3.2(275)
 atom, § 1.7.1(58), § 1.10(90), § 6.1(441), § 6.3.1(470)
 atom density, § 6.1(441), § 6.2(459)
 atom positions, § 6.1(441)
 atomic, § 1.1(3)
 atomic emission spectroscopy, § 1.2(17)
 atomic fluorescence spectroscopy, § 1.7.2(60)
 atomic force microscopy, § 8.2(634)
 atomizer, § 1.1(3)
 atomizers, § 1.1(3)
 Auger, § 1.9(84)
 axis, § 6.3.2(479)

- B** band gap, § 3.5.1(295), § 7.4.2(580), § 7.4.4(599)
 battery, § 9.1(661)
 beam, § 1.9(84), § 3.2.3(259)
 beam splitter, § 3.3.3(276)
 beamline, § 1.6(47)
 BEEM, § 7.3.2(567)
 Beer Lambert Law, § 7.4.3(588)
 Beer-Lambert, § 7.4.4(599)
 Beer-Lambert law, § 2.5.2(160)
 bend, § 3.3.2(275)
 Bennett, § 6.7(518)
 benzene, § 3.3.2(275), § 3.4.1(288)
 benzyl acetate, § 3.7.4(336)
 BET, § 2.7(185), § 7.5(608)
 beta, § 1.13(111)
 Binning, § 7.3.1(560), § 7.3.2(567)
 biological, § 1.1(3)
 biological Samples, § 3.10(380)
 biotite, § 1.10(90)
 birefringence, § 6.8(526)
 bismuth, § 1.13(111)
 blue, § 6.8(526)
 body-centered, § 6.1(441)
 Bohr, § 7.4.2(580)
 Boltzmann, § 7.5(608)
 borate, § 6.3.2(479)
 boron, § 6.3.2(479)
 bracket, § 1.1(3)
 bracketing, § 1.1(3)
 Bragg, § 6.3.1(470), § 6.4(492)
 Bravais lattice, § 6.1(441)
 breadboard, § 9.1(661)
 broadening, § 3.7.5(340)
 Brunauer, § 2.7(185)
 Brunner, § 7.5(608)
 BSED, § 8.3(639)
 buffer, § 6.6(509)
 bulk, § 6.1(441)
 bulk material, § 1.8.1(75)
 burn, § 1.4(28)
 capillary, § 4.1(397), § 6.7(518)
 carbon, § 1.4(28), § 3.7.1(321), § 3.9.1(365), § 8.2(634), § 9.1(661)
 carbon monoxide, § 8.4(650)
 carbon nanotube, § 3.2.2(245)
 carbonyl, § 3.3.3(276)
 carpet, § 9.1(661)
 Carr, § 7.5(608)
 carrier gas, § 4.1(397)
 catalysis, § 8.4(650)
 catalyst, § 2.5.1(154), § 7.5(608), § 8.4(650)
 CCD, § 3.2.3(259)
 CD, § 6.6(509)
 CdS, § 7.4.3(588)
 CdSe, § 7.4.2(580), § 7.4.3(588), § 9.1(661)
 CdTe, § 7.4.3(588)
 cell, § 1.7.1(58), § 2.7(185), § 6.6(509)
 CHA, § 1.9(84)
 Chadwick, § 6.4(492)
 chalcogenide, § 2.5.3(172)
 chalcopyrite, § 6.1(441), § 6.2(459)
 chamber, § 4.3(413)
 characterization, § 2.1(119), § 3.5.2(304), § 7.5(608)
 characterization techniques, § 1.6(47), § 6.5.1(502)
 charge transfer, § 1.7.3(61)
 chemical, § 5.1(425), § 6.6(509)
 chemical ionization, § 3.11.1(388)
 chemical vapor deposition, § 2.5.3(172)
 chemistry, § (1), § 1.8.1(75), § 2.1(119), § 3.3.3(276), § 3.10(380), § 7.5(608)
 chiral, § 6.6(509), § 6.8(526)
 chromatography, § 3.10(380), § 4.1(397)
 cinnabar, § 6.1(441)
 circular dichroism, § 6.6(509)
 cis, § 3.3.2(275)
 Cisneros, § 1.13(111)
 Clausius-Clapeyron, § 2.5.3(172)
 close packed, § 6.1(441)
 CMA, § 1.9(84)
 CNT, § 3.2.2(245), § 7.2.3(552), § 9.1(661)
 CO, § 3.3.3(276)
 CO₂, § 2.5.1(154), § 2.5.2(160)
 cobalt, § 1.2(17)
 cold, § 1.7.1(58), § 1.7.2(60)
 colligative, § 2.2(123)
 colloid, § 7.3.2(567)
 column, § 2.4(144), § 4.1(397), § 4.2(408)
 combustion, § 1.4(28)
 complexe, § 2.5.3(172)
C C60, § 5.2(429), § 7.2.3(552)
 cadmium, § 7.4.2(580), § 7.4.3(588), § 7.4.4(599)
 cadmium selenide, § 7.4.2(580), § 7.4.4(599)
 calcium, § 2.2(123)
 calibration, § 1.1(3), § 3.4.1(288)
 calomel, § 2.8(196)
 calorimetry, § 2.6(180)
 camera, § 6.3.1(470)
 cantilever, § 8.2(634)

- composition, § 2.6(180)
- compound, § 2.5.3(172), § 6.1(441)
- concentration, § 1.5(43)
- concentric, § 1.9(84)
- condensor, § 8.3(639)
- conduction band, § 7.4.2(580), § 7.4.4(599)
- conductivity, § 8.4(650)
- conductor, § 7.3.2(567)
- confocal, § 7.1(535)
- constraint, § 6.3.2(479)
- contrast, § 2.9(206), § 6.8(526)
- contrast agent, § 2.9(206)
- Coopers, § 3.1.2(225)
- coordination number, § 6.1(441), § 6.5.1(502)
- copper, § 1.2(17), § 1.4(28), § 3.8.2(359),
§ 6.1(441), § 6.3.2(479), § 8.3(639)
- core, § 1.10(90)
- coronene, § 3.5.2(304)
- coupling, § 3.7.3(329), § 3.7.5(340),
§ 3.8.1(355)
- coupling constant, § 3.7.1(321)
- CPMG, § 7.5(608)
- cro-SEM, § 8.3(639)
- cryoscopy, § 2.2(123)
- crystal, § 6.1(441), § 6.3.1(470)
- crystal axes, § 6.1(441)
- crystal direction, § 6.1(441)
- crystal plane, § 6.1(441)
- crystalline, § 6.3.1(470)
- crystallographic, § 6.3.2(479)
- Crystallography, § 1.12(106), § 6.1(441),
§ 6.3.1(470)
- cubane, § 2.5.3(172)
- cubic, § 6.1(441), § 6.2(459)
- current, § 2.8(196), § 7.3.2(567), § 9.1(661)
- current mode, § 7.3.1(560)
- Currie Law, § 3.1.1(213)
- curve, § 1.1(3)
- curves, § 1.1(3)
- curvette, § 7.4.3(588)
- cuvette, § 3.4.1(288), § 6.6(509)
- CV, § 2.8(196)
- CV-AFS, § 1.7.2(60)
- CVAFS, § 1.7.1(58)
- CVD, § 2.5.3(172)
- cyanine, § 3.5.2(304)
- cyclic voltammetry, § 2.8(196)
- cylindrical, § 1.9(84)
- cytochrome, § 6.7(518)
- de Broglie, § 6.4(492)
- decay, § 1.13(111)
- decomposition, § 2.5.3(172)
- defect, § 3.5.1(295), § 6.1(441)
- depth, § 1.9(84)
- depth resolution, § 1.11(98)
- detection, § 1.2(17), § 1.3(24), § 1.9(84),
§ 3.5.2(304), § 3.10(380)
- detection limit, § 1.11(98)
- detector, § 1.7.1(58), § 1.7.3(61), § 1.8.2(80),
§ 1.9(84), § 3.3.3(276), § 4.1(397), § 4.2(408),
§ 6.3.1(470), § 6.4(492), § 7.1(535), § 8.3(639),
§ 8.4(650)
- Dewar, § 2.7(185)
- diamagnetic, § 3.1.1(213), § 3.7.6(347)
- diamond, § 6.1(441), § 6.2(459)
- diastereomer, § 3.7.4(336)
- differential scanning calorimetry, § 2.6(180)
- differential thermal analysis, § 2.5.3(172)
- diffraction, § 6.3.1(470), § 6.4(492)
- diffractometer, § 6.3.1(470)
- dipolar, § 3.7.5(340)
- disc, § 2.8(196)
- discotic, § 6.8(526)
- dislocation, § 6.1(441)
- disorder, § 1.12(106), § 6.3.2(479), § 7.6(619)
- dispersion, § 8.4(650)
- dispersive, § 1.10(90)
- display, § 6.8(526)
- DMF, § 3.4.1(288)
- DNA, § 3.5.2(304)
- Dole, § 6.7(518)
- doublet, § 3.7.1(321), § 3.7.3(329)
- DSC, § 2.5.2(160), § 2.6(180)
- DTA, § 2.5.1(154), § 2.5.3(172)
- Dumas, § 1.4(28)
- dynamic, § 5.1(425), § 6.3.2(479)
- dynamics, § 3.3.4(283)
- E** EDX, § 1.10(90), § 1.11(98)
- efficiency, § 4.1(397)
- electothermal, § 1.1(3)
- electro ionization spray, § 3.10(380)
- electrode, § 1.5(43), § 2.8(196)
- electrolyte, § 1.5(43)
- electron, § 1.9(84), § 1.10(90), § 2.8(196),
§ 7.2.1(542), § 7.2.2(550), § 7.3.2(567),
§ 7.4.2(580), § 8.3(639)
- electron impact, § 3.11.1(388)
- electron paramagnetic resonance, § 3.8.1(355),
§ 3.8.2(359)
- electron spin resonance, § 3.8.1(355),
- D** D-band, § 3.2.2(245)
- dangling bond, § 6.1(441), § 6.2(459)

- § 3.8.2(359)
 - electronic environment, § 6.5.1(502)
 - electrospray, § 3.11.1(388), § 6.7(518)
 - electrospray ionization quadrupole
 - time-of-flight mass spectrometry, § 3.10(380)
 - element, § 1.10(90), § 3.7.2(326), § 6.1(441)
 - elemental, § 3.9.1(365)
 - elemental analysis, § 3.11.1(388)
 - ellipticity, § 6.6(509)
 - emission, § 1.7.3(61), § 3.5.1(295)
 - Emmet, § 7.5(608)
 - Emmett, § 2.7(185)
 - empirical, § 1.4(28)
 - enantiomer, § 3.7.4(336)
 - endothermic, § 2.6(180)
 - energy, § 1.10(90), § 7.4.2(580)
 - enthalpy, § 2.5.3(172)
 - entropy, § 2.5.3(172)
 - environment, § 1.7.3(61)
 - environmental, § 1.1(3)
 - environmental protection, § 3.10(380)
 - epitaxy, § 6.1(441)
 - EPR, § 3.8.1(355), § 3.8.2(359)
 - equilibrium, § 5.1(425)
 - erythrose, § 3.7.4(336)
 - ESCA, § 3.9.1(365)
 - ESI, § 3.10(380), § 3.11.1(388), § 6.7(518)
 - ESI-MS, § 3.10(380)
 - ESI-QTOF-MS, § 3.10(380)
 - ESR, § 3.8.1(355), § 3.8.2(359)
 - ethanol, § 3.4.1(288), § 3.7.1(321)
 - ethyl formate, § 3.7.4(336)
 - ethyl selenocyanate, § 3.3.4(283)
 - ethyl thiocyanate, § 3.3.4(283)
 - europium, § 3.7.6(347)
 - EXAFS, § 1.6(47), § 6.5.1(502)
 - EXAFS equation, § 6.5.1(502)
 - excitation, § 7.4.4(599)
 - excited state, § 7.1(535)
 - excited states, § 3.5.1(295)
 - exciton, § 7.4.2(580)
 - exothermic, § 2.6(180)
 - experiment, § 9.1(661)
 - extended X-ray absorption fine structure, § 1.6(47), § 6.5.1(502)
 - extinction, § 6.6(509)
- F**
- FAB, § 3.11.1(388)
 - face-centered, § 6.1(441)
 - fan, § 9.1(661)
 - fast atom bombardment, § 3.11.1(388)
 - Fe, § 3.6.3(318)
 - Fe₃O₄, § 3.6.2(317)
 - feedback, § 7.3.1(560)
 - Fenn, § 6.7(518)
 - Fermi, § 7.3.2(567)
 - ferromagnetic, § 3.1.1(213)
 - fiber, § 7.3.2(567)
 - field, § 3.7.1(321), § 3.7.6(347)
 - filter, § 1.7.3(61), § 7.1(535)
 - first-order, § 3.7.3(329)
 - flame, § 1.1(3), § 1.4(28)
 - flow, § 8.4(650)
 - fluorescence, § 1.6(47), § 1.7.1(58), § 1.7.3(61), § 3.5.1(295), § 3.5.2(304), § 6.5.1(502), § 7.1(535), § 7.4.4(599)
 - fluorescence resonance energy transfer, § 1.7.3(61)
 - fluoride, § 1.5(43)
 - fluorine, § 2.5.3(172), § 3.9.1(365), § 6.3.2(479)
 - fluorophore, § 1.7.3(61)
 - fluorophores, § 7.1(535)
 - fluxoid, § 3.1.2(225)
 - focal length, § 8.3(639)
 - food safety, § 3.10(380)
 - forensics, § 1.13(111)
 - formula, § 1.4(28)
 - fourier-transform, § 3.3.1(261)
 - Fpt, § 2.2(123)
 - framework, § 2.7(185)
 - free path, § 8.3(639)
 - freezing, § 2.2(123)
 - frequency, § 3.7.2(326), § 3.7.4(336)
 - FRET, § 1.7.3(61)
 - Friedrich, § 6.3.1(470)
 - FT-IR, § 3.3.1(261)
 - FTIR, § 2.5.2(160), § 3.3.3(276)
 - fuel, § 1.4(28)
 - fullerene, § 7.6(619)
 - functional group, § 2.5.1(154), § 3.3.4(283)
 - functionalization, § 3.9.1(365)
 - Functionalized SWNTs, § 2.5.1(154)
- G**
- G value, § 3.8.1(355)
 - G-band, § 3.2.2(245)
 - GaAs, § 6.2(459), § 7.3.2(567)
 - gallium, § 2.5.3(172), § 6.1(441), § 6.2(459)
 - gamma, § 1.13(111)
 - gamma-ray, § 1.13(111)
 - gas, § 2.5.3(172), § 2.7(185), § 4.1(397), § 4.3(413), § 8.4(650)
 - gas chromatography, § 4.2(408)
 - gas constant, § 1.5(43), § 2.5.3(172)
 - Gay-Lussac, § 1.4(28)

- GC, § 4.1(397), § 4.2(408)
 GC-MS, § 3.11.1(388)
 Ge, § 6.2(459)
 gel permeation chromatography, § 2.4(144)
 geochemistry, § 1.3(24)
 geological, § 1.1(3)
 geology, § 1.3(24)
 germanium, § 6.1(441)
 germanium, § 6.2(459)
 GFP, § 3.5.2(304)
 Gill, § 7.5(608)
 glass, § 3.4.1(288)
 gold, § 1.7.2(60), § 2.8(196), § 3.2.1(241),
 § 3.2.3(259), § 4.2(408), § 7.3.2(567)
 graphene, § 7.2.3(552), § 7.3.1(560), § 7.6(619)
 graphite, § 2.8(196), § 3.9.1(365), § 7.6(619)
 ground state, § 7.1(535)
 Group 12, § 7.4.2(580), § 7.4.3(588),
 § 7.4.4(599)
 Group 12-16, § 6.1(441)
 Group 13-15, § 6.1(441)
 Group 16, § 7.4.2(580), § 7.4.3(588),
 § 7.4.4(599)
 Group II-VI, § 6.1(441)
 Group III-V, § 6.1(441)
- H** hand, § 6.6(509)
 hazards, § 3.10(380)
 He, § 1.11(98)
 headspace, § 4.1(397), § 4.2(408)
 heat, § 2.1(119)
 height, § 7.3.2(567)
 height mode, § 7.3.1(560)
 helium, § 1.7.3(61), § 1.11(98), § 2.7(185),
 § 3.7.5(340), § 8.4(650)
 helix, § 6.6(509)
 hemispherical, § 1.9(84)
 hexagon, § 6.1(441)
 hexagonal, § 6.1(441)
 hexanol, § 3.7.6(347)
 hfac, § 2.5.3(172)
 Hg, § 1.7.2(60)
 high pressure, § 3.5.2(304)
 Hinckley, § 3.7.6(347)
 history, § 1.1(3)
 hole, § 7.4.2(580)
 hopping, § 5.2(429)
 hybridization, § 3.9.1(365)
 hydrochlorination, § 4.2(408)
 hydrogen, § 1.4(28), § 2.5.3(172), § 3.7.1(321),
 § 7.5(608), § 8.4(650)
 hydroxide, § 3.7.1(321)
 Hyperfine, § 3.8.1(355)
- I** I-V plot, § 9.1(661)
 ICP, § 1.2(17), § 3.11.1(388)
 ICP-AES, § 1.2(17)
 ICP-MS, § 1.2(17), § 1.3(24)
 ICT, § 1.7.3(61)
 II-VI, § 7.4.2(580), § 7.4.4(599)
 image, § 6.8(526), § 8.3(639)
 imaging, § 2.9(206)
 impurity, § 3.5.1(295)
 indices, § 6.1(441)
 indium, § 6.1(441), § 6.2(459), § 7.3.2(567)
 infra red, § 3.3.3(276)
 infrared, § 3.3.1(261), § 4.3(413)
 InGaAs, § 1.7.3(61)
 injection, § 2.7(185)
 inorganic, § (1)
 Inorganic Nanotechnology, § 3.1.3(234)
 InP, § 6.2(459)
 instrument, § 1.10(90)
 instrumentation, § 1.9(84)
 inter-atomic, § 6.1(441)
 interaction, § 3.7.5(340), § 4.3(413)
 interference, § 1.1(3)
 interferences, § 1.1(3)
 interferometer, § 3.3.3(276)
 interstitial, § 6.1(441)
 intra-planar, § 6.1(441)
 intramolecular, § 1.7.3(61)
 inventor, § 6.4(492)
 inversion, § 6.3.2(479)
 ion, § 1.7.3(61)
 ion selective electrode, § 1.5(43)
 ion trap, § 3.11.1(388)
 ionic pump, § 4.3(413)
 ionization, § 6.7(518)
 IR, § 3.3.2(275), § 3.3.3(276)
 iron, § 1.2(17), § 1.4(28), § 2.5.1(154),
 § 3.6.2(317)
 Iron oxide, § 3.6.3(318), § 3.6.4(320),
 § 6.5.1(502)
 ISE, § 1.5(43)
 isomer shift, § 3.6.3(318)
 isotherm, § 2.7(185), § 4.3(413)
 isothermal, § 2.5.3(172)
 isotope, § 3.7.1(321)
 Isotropic, § 3.8.1(355)
- J** Jablonski, § 1.7.3(61)
 jacket, § 3.7.5(340)
 junction, § 9.1(661)

- K** K shell, § 1.9(84)
 kinetic energy, § 1.9(84)
 kinetics, § 2.5.3(172)
 Knipping, § 6.3.1(470)
- L** L shell, § 1.9(84)
 LaB6, § 8.3(639)
 laminar, § 1.4(28)
 lamp, § 3.5.2(304), § 6.6(509)
 Langmuir, § 2.7(185), § 4.3(413)
 lanthanide, § 3.7.6(347)
 Larmor, § 7.5(608)
 laser, § 3.2.3(259), § 7.1(535), § 7.6(619)
 lattice, § 6.1(441), § 6.4(492)
 lattice constant, § 6.2(459)
 lattice parameter, § 6.1(441), § 6.2(459)
 Lavoisier, § 1.4(28)
 layer, § 7.2.2(550), § 7.6(619)
 LC, § 3.10(380), § 6.8(526)
 LC-MS, § 3.10(380), § 3.11.1(388)
 LC/ESI-QTOF-MS, § 3.10(380)
 LD, § 6.6(509)
 lead, § 1.13(111)
 left, § 6.6(509)
 lens, § 3.2.3(259), § 8.3(639)
 level, § 1.10(90)
 Liebig, § 1.4(28)
 lifetime, § 3.3.4(283)
 ligand, § 3.3.3(276)
 light, § 1.7.1(58), § 3.3.3(276), § 6.6(509),
 § 6.8(526), § 7.3.2(567), § 9.1(661)
 limitation, § 1.9(84)
 line broadening, § 3.7.5(340)
 linear dichroism, § 6.6(509)
 liquid, § 1.5(43), § 2.6(180), § 3.7.5(340),
 § 7.3.1(560)
 liquid chromatography, § 3.10(380)
 liquid crystal, § 6.8(526)
 lithography, § 9.1(661)
 luminescence, § 3.5.1(295)
 lyotropic, § 6.8(526)
- M** M shell, § 1.9(84)
 magic angle, § 3.7.5(340)
 magnesium, § 1.10(90)
 magnetic, § 2.9(206), § 3.1.2(225), § 3.6.3(318),
 § 3.7.1(321), § 3.7.6(347), § 6.4(492)
 magnetic circular dichroism, § 6.6(509)
 Magnetic field, § 3.8.1(355), § 7.5(608)
 magnetic moment, § 3.1.1(213)
 magnetic resonance imaging, § 2.9(206)
 Magnetism, § 3.1.1(213), § 3.1.3(234)
 magnetite, § 3.6.2(317), § 3.6.3(318)
 magnification, § 8.3(639)
 MALDI, § 3.11.1(388), § 6.7(518)
 manifold, § 2.7(185)
 manipulator, § 4.3(413)
 marine, § 1.1(3)
 mass, § 6.7(518)
 mass spectrometer, § 3.10(380), § 4.3(413)
 mass spectrometry, § 1.2(17), § 3.10(380),
 § 3.11.1(388)
 mass spectroscopy, § 1.3(24)
 material, § 7.2.2(550), § 8.4(650), § 9.1(661)
 materials, § (1)
 materials science, § 1.6(47), § 6.5.1(502)
 matrix assisted laser desorption ionization,
 § 3.11.1(388)
 matrix effects, § 3.10(380)
 MCD, § 6.6(509)
 mechanism, § 3.8.2(359)
 Meiboom, § 7.5(608)
 melting, § 2.1(119), § 2.2(123)
 membrane, § 1.5(43)
 mercury, § 1.7.2(60), § 1.7.3(61), § 2.8(196),
 § 3.5.2(304)
 mercury sulfide, § 6.2(459)
 metal, § 1.3(24), § 1.8.2(80), § 3.3.3(276),
 § 7.3.1(560), § 8.4(650)
 metal organic chemical vapor deposition,
 § 2.5.3(172)
 Metal oxide, § 2.5.2(160)
 metal-organic, § 2.7(185)
 metallic and semiconducting nanotubes,
 § 3.2.2(245)
 metallization, § 9.1(661)
 metalloproteins, § 6.7(518)
 metallotropic, § 6.8(526)
 methyl, § 3.7.1(321)
 microscope, § 3.2.3(259), § 6.8(526), § 7.1(535)
 microscopy, § 1.9(84), § 6.8(526), § 7.1(535),
 § 7.2.1(542), § 7.2.2(550), § 7.3.1(560),
 § 7.3.2(567), § 8.3(639)
 Miller, § 6.1(441)
 Minamata, § 1.7.3(61)
 mineral, § 1.3(24)
 mirror, § 1.9(84), § 3.3.3(276), § 6.3.2(479),
 § 7.1(535)
 Mitchell, § 6.4(492)
 MOCVD, § 2.5.3(172)
 mode, § 1.6(47), § 6.5.1(502)
 molecular, § 1.4(28)
 molecular beacon, § 3.5.2(304)

- molecular weight, § 2.4(144), § 8.4(650)
 - molecular weight distribution, § 2.4(144)
 - molecule, § 1.7.3(61), § 2.3(129), § 3.3.3(276), § 3.7.4(336)
 - molybdenite, § 1.10(90)
 - molybdenum, § 1.10(90)
 - monochromator, § 1.7.1(58), § 1.7.3(61), § 3.2.3(259), § 3.5.2(304)
 - monoclinic, § 6.1(441)
 - monolayer, § 2.7(185)
 - morphology, § 8.1(623), § 8.2(634)
 - Mosher, § 3.7.4(336)
 - Mossbauer, § 3.6.3(318), § 3.6.4(320)
 - mossbauer effect, § 3.6.1(315)
 - Mossbauer spectroscopy, § 3.6.1(315)
 - motor, § 5.1(425)
 - Mp, § 2.2(123)
 - MRI, § 2.9(206)
 - MS, § 3.10(380), § 3.11.1(388)
 - MS analysis, § 3.10(380)
 - multi-walled nanotubes, § 3.2.2(245)
 - multiplet, § 3.7.3(329)
 - MWNT, § 3.2.2(245), § 7.2.3(552)
- N**
- n-type, § 7.3.2(567)
 - nano, § (1), § 3.9.1(365), § 7.2.2(550), § 7.3.1(560), § 7.4.2(580), § 7.4.4(599), § 8.2(634), § 8.3(639)
 - nanocar, § 5.2(429)
 - nanodiamond, § 3.9.1(365)
 - nanomaterial, § 3.9.1(365), § 7.2.3(552), § 7.3.1(560)
 - nanoparticle, § 2.7(185), § 3.2.1(241), § 3.2.3(259), § 3.4.1(288), § 3.6.2(317), § 3.6.3(318), § 3.6.4(320), § 4.2(408), § 7.4.1(577), § 7.4.2(580), § 7.4.3(588), § 7.4.4(599), § 7.5(608), § 8.3(639)
 - nanoparticles, § 1.2(17), § 1.8.2(80), § 2.5.2(160)
 - nanotechnology, § 1.2(17)
 - nanotube, § 2.5.1(154), § 7.2.3(552), § 7.3.1(560), § 7.6(619), § 9.1(661)
 - natural abundance, § 3.7.2(326)
 - Nb, § 1.11(98)
 - nematic, § 6.8(526)
 - Nernst, § 1.5(43)
 - neutron, § 6.4(492)
 - Newman, § 3.7.4(336)
 - nicotine, § 2.2(123)
 - niobium, § 1.11(98)
 - nitrate, § 2.2(123)
 - nitride, § 6.2(459)
 - nitrogen, § 1.4(28), § 2.5.3(172), § 2.7(185), § 2.8(196), § 3.7.5(340), § 6.6(509)
 - nMag, § 3.6.2(317)
 - NMR, § 2.5.2(160), § 2.9(206), § 3.7.1(321), § 3.7.2(326), § 3.7.3(329), § 3.7.4(336), § 3.7.5(340), § 3.7.6(347), § 5.1(425), § 6.6(509), § 7.5(608)
 - non-evaporate pump, § 4.3(413)
 - non-stoichiometric, § 3.6.4(320)
 - Nonstoichiometric, § 3.6.3(318)
 - nuclear, § 1.13(111), § 2.9(206), § 3.7.1(321), § 3.7.5(340)
 - nuclear magnetic resonance, § 2.9(206), § 3.7.3(329), § 3.7.4(336), § 3.7.5(340), § 3.7.6(347), § 7.5(608)
 - nuclei, § 3.7.1(321), § 3.8.1(355)
 - nucleus, § 3.7.3(329)
- O**
- O'Neill, § 2.6(180)
 - Oak Ridge, § 6.4(492)
 - object, § 8.3(639)
 - octahedral, § 6.1(441)
 - olefin, § 6.3.2(479)
 - optical, § 6.6(509), § 6.8(526), § 7.3.2(567), § 7.4.2(580)
 - orbital, § 1.9(84)
 - organic, § 1.4(28)
 - orientation, § 6.1(441)
 - orthorhombic, § 6.1(441)
 - osmium, § 8.3(639)
 - output, § 1.7.1(58)
 - oxidation, § 2.6(180), § 3.8.2(359)
 - Oxidation state, § 3.6.3(318)
 - oxide, § 2.7(185), § 7.3.2(567)
 - oxidize, § 1.4(28)
 - oxygen, § 6.6(509)
 - ozone, § 6.6(509)
- P**
- p-type, § 1.11(98), § 7.3.2(567)
 - palladium, § 4.2(408), § 8.4(650)
 - pan, § 2.6(180)
 - paramagnetic, § 3.1.1(213), § 3.1.2(225), § 3.8.1(355)
 - Pascal, § 3.7.1(321)
 - path length, § 6.6(509)
 - PCE, § 4.2(408)
 - Pd, § 8.4(650)
 - peak, § 1.9(84), § 4.1(397), § 4.2(408)
 - PEI, § 2.5.1(154)
 - pentane, § 4.2(408)
 - perchloroethylene, § 4.2(408)
 - Perkin-Elmer, § 2.6(180)

PET, § 1.7.3(61)
 phase, § 6.8(526)
 phenylalanine, § 3.5.2(304)
 phosphide, § 6.1(441), § 6.2(459)
 phosphorescence, § 3.5.1(295)
 photoelectric effect, § 1.6(47)
 photoelectron, § 1.8.1(75), § 1.8.2(80),
 § 1.9(84), § 3.9.1(365)
 photoinduced electron transfer, § 1.7.3(61)
 photoluminescence, § 3.5.1(295)
 photoluminescence spectroscopy, § 3.5.1(295)
 photon, § 1.7.1(58), § 3.5.1(295), § 7.1(535),
 § 7.4.4(599)
 photoresponse, § 9.1(661)
 photovoltaic, § 9.1(661)
 Physics Chemistry, § 3.1.3(234)
 pivoting, § 5.2(429)
 Plank, § 7.5(608)
 plasma, § 4.3(413)
 plastic, § 3.4.1(288), § 7.4.3(588)
 platinum, § 2.8(196), § 8.3(639)
 point, § 2.1(119), § 6.1(441)
 polarized, § 6.6(509), § 6.8(526)
 polarized optical microscope, § 6.8(526)
 poly(thiophene ester), § 8.3(639)
 polydisperse, § 2.4(144)
 polyethylene, § 8.3(639)
 polymer, § 2.3(129), § 2.4(144), § 8.3(639)
 polystyrene, § 8.3(639)
 POM, § 6.8(526)
 potassium, § 1.10(90)
 potentiometer, § 9.1(661)
 powder, § 1.8.2(80)
 Powers, § 6.4(492)
 ppm, § 3.7.1(321), § 3.7.4(336)
 precursor, § 3.6.2(317)
 Pregl, § 1.4(28)
 premixed, § 1.4(28)
 preparation, § 1.1(3), § 3.3.1(261), § 7.2.1(542)
 pressure, § 2.7(185)
 pretreatment, § 1.1(3)
 principle, § 7.2.1(542)
 profiling, § 1.9(84)
 projector, § 9.1(661)
 property, § 2.2(123)
 propyl cyanide, § 3.3.4(283)
 protactinium, § 1.13(111)
 protein, § 3.5.2(304), § 6.6(509)
 proteins, § 6.7(518)
 proton, § 3.7.1(321), § 3.7.4(336), § 5.1(425),
 § 7.5(608)

Prout, § 1.4(28)
 PSTM, § 7.3.2(567)
 pump-probe, § 3.3.4(283)
 Purcell, § 7.5(608)
 purity, § 2.1(119), § 2.6(180)
 pyrene, § 3.5.2(304)
 pyrolysis, § 2.5.2(160)

Q QD, § 7.4.1(577)
 QTOF-MS, § 3.10(380)
 quadrupole, § 3.10(380), § 3.11.1(388),
 § 4.3(413), § 6.7(518)
 quantum dot, § 7.4.2(580), § 7.4.3(588),
 § 7.4.4(599)
 quantum dots, § 7.4.1(577)
 quartet, § 3.7.1(321), § 3.7.3(329)
 quartz, § 3.4.1(288), § 7.4.3(588)
 quaternary, § 6.2(459)
 quinolone, § 3.10(380)

R Radial breathing mode, § 3.2.2(245)
 radiation, § 1.7.1(58), § 3.5.1(295), § 6.3.1(470)
 radium, § 1.13(111)
 Raman, § 2.5.2(160), § 3.2.1(241), § 3.2.3(259),
 § 7.6(619)
 Raman spectroscopy, § 3.2.2(245)
 ray, § 1.13(111)
 Rayleigh, § 2.4(144), § 3.2.1(241)
 RBS, § 1.11(98)
 reaction order, § 4.3(413)
 receptivity, § 3.7.2(326)
 recombination mechanisms, § 3.5.1(295)
 Refinement, § 1.12(106), § 6.3.2(479)
 reflection, § 4.3(413)
 reflection absorption infrared spectrometer
 (RAIRS), § 4.3(413)
 relaxation, § 2.9(206)
 relaxometer, § 2.9(206)
 requirements, § 1.6(47)
 resistor, § 9.1(661)
 resolution, § 1.9(84), § 4.1(397)
 resonance, § 2.9(206), § 3.7.1(321)
 resonant, § 3.5.1(295)
 restraint, § 6.3.2(479)
 retention, § 4.1(397)
 rhodamine, § 3.5.2(304)
 rhombohedral, § 6.1(441)
 right, § 6.6(509)
 rock salt, § 6.1(441)
 Rohrer, § 7.3.1(560), § 7.3.2(567)
 rolling, § 5.2(429)
 Rose Bengal, § 3.4.1(288)

- rotation, § 6.3.2(479), § 6.6(509)
- rudolf mossbauer, § 3.6.1(315)
- ruthenium, § 8.3(639)
- Rutherford, § 1.11(98)
- Röntgen, § 6.3.1(470)
- S**
 - sample, § 1.1(3), § 1.6(47), § 2.1(119), § 3.3.1(261), § 3.3.3(276), § 7.2.2(550)
 - sample preparation, § 1.8.2(80)
 - sample preparation methods,, § 3.10(380)
 - samples, § 1.1(3)
 - Sanders, § 3.7.6(347)
 - scan, § 6.3.1(470)
 - scan coil, § 8.3(639)
 - scanning, § 1.9(84), § 8.3(639)
 - scanning tunneling microscopy, § 7.3.1(560), § 7.3.2(567)
 - scattering, § 3.2.1(241), § 6.4(492)
 - Scrodinger, § 7.4.2(580)
 - second-order, § 3.7.3(329)
 - sector, § 3.11.1(388)
 - selenide, § 6.2(459), § 7.4.3(588)
 - selenium, § 6.2(459), § 7.4.2(580), § 7.4.3(588), § 7.4.4(599)
 - SEM, § 1.9(84), § 8.1(623), § 8.3(639)
 - semiconductor, § 6.1(441), § 6.2(459), § 7.3.2(567), § 7.4.2(580), § 7.4.3(588), § 7.4.4(599)
 - sensitivity, § 3.10(380)
 - sensor, § 1.7.3(61)
 - separation, § 4.1(397)
 - sequence, § 6.6(509)
 - SERS, § 3.2.3(259)
 - sheet, § 6.6(509)
 - shift, § 1.7.3(61), § 3.7.1(321), § 3.7.4(336)
 - Shull, § 6.4(492)
 - Si, § 6.2(459)
 - silica, § 7.5(608)
 - silicon, § 1.10(90), § 1.11(98), § 6.1(441), § 6.2(459), § 7.4.1(577)
 - silver, § 1.5(43), § 2.8(196), § 8.3(639)
 - single stage accelerator, § 1.11(98)
 - single walled carbon nanotubes, § 7.2.3(552)
 - Single-walled nanotubes, § 3.2.2(245)
 - singlet, § 3.7.1(321), § 3.7.3(329)
 - site, § 2.7(185)
 - size, § 8.4(650)
 - size exclusion, § 2.4(144)
 - sliding, § 5.2(429)
 - smatic, § 6.8(526)
 - Sn, § 6.2(459)
 - solar cell, § 9.1(661)
 - solid, § 2.6(180), § 2.7(185), § 3.7.5(340), § 4.3(413)
 - solid phase micro-extraction, § 3.10(380)
 - solid solution, § 1.12(106), § 6.2(459)
 - solid state, § 3.7.5(340), § 6.1(441)
 - solvent, § 3.2.3(259), § 3.4.1(288), § 3.7.4(336), § 7.4.3(588)
 - source, § 1.9(84)
 - sources, § 6.4(492)
 - SP-STM, § 7.3.2(567)
 - spectra, § 1.8.1(75), § 3.7.4(336)
 - spectrometer, § 1.1(3), § 3.3.3(276), § 3.7.6(347), § 4.3(413)
 - spectrometry, § 6.7(518)
 - spectroscopy, § 1.1(3), § 1.6(47), § 1.7.1(58), § 1.7.3(61), § 1.8.1(75), § 1.8.2(80), § 1.9(84), § 1.10(90), § 1.13(111), § 3.2.1(241), § 3.2.3(259), § 3.3.1(261), § 3.3.2(275), § 3.4.1(288), § 3.5.1(295), § 3.6.4(320), § 3.7.1(321), § 3.7.4(336), § 3.8.1(355), § 3.8.2(359), § 3.9.1(365), § 6.6(509), § 7.4.1(577), § 7.4.3(588), § 7.4.4(599), § 7.6(619)
 - spectrum, § 1.9(84), § 1.11(98), § 6.6(509), § 9.1(661)
 - spin, § 3.7.3(329), § 3.7.5(340)
 - Spin-spin, § 3.8.1(355)
 - spinel, § 3.6.4(320)
 - splitting, § 3.7.3(329)
 - SPME, § 3.10(380)
 - sputter, § 1.8.1(75), § 1.8.2(80)
 - sputtering, § 1.8.1(75), § 1.8.2(80), § 1.9(84), § 4.3(413)
 - SQUID, § 3.1.2(225)
 - stability, § 2.6(180)
 - standard, § 1.1(3)
 - state, § 1.7.3(61)
 - static, § 6.3.2(479)
 - stationary phase, § 4.1(397)
 - Steno, § 6.3.1(470)
 - stereoisomer, § 3.7.4(336)
 - STM, § 5.2(429), § 7.3.1(560), § 7.3.2(567)
 - stoichiometric, § 6.2(459)
 - stoichiometric ratio, § 1.11(98)
 - Stokes, § 3.2.1(241), § 3.5.2(304)
 - stretch, § 3.3.2(275)
 - structure, § 3.5.1(295), § 6.1(441), § 6.6(509), § 8.1(623)
 - sublimation, § 2.5.3(172)
 - sublime, § 2.5.3(172)
 - substitution, § 6.1(441)

- substrate, § 1.8.2(80)
 - sulfide, § 6.1(441), § 6.2(459)
 - sulfur, § 1.10(90), § 6.2(459), § 7.4.2(580), § 7.4.3(588), § 7.4.4(599)
 - Superconducting Quantum Interference Device, § 3.1.2(225)
 - Superconducting Quantum Interference Device, § 3.1.3(234)
 - support, § 4.1(397), § 8.4(650)
 - surface, § 1.9(84), § 2.7(185), § 3.2.1(241), § 3.2.3(259), § 3.5.1(295), § 3.9.1(365), § 5.2(429), § 6.1(441), § 7.3.2(567), § 8.1(623), § 8.2(634), § 8.4(650)
 - surface area, § 7.5(608)
 - surface chemistry, § 4.3(413)
 - surface-enhanced Raman spectroscopy, § 3.2.1(241), § 3.2.3(259)
 - surfactant, § 1.8.1(75), § 3.6.2(317)
 - SWNT, § 2.5.1(154), § 3.2.2(245), § 3.9.1(365), § 7.2.3(552), § 7.3.1(560)
 - symmetric, § 3.3.2(275)
 - symmetry, § 4.1(397)
 - synchrotron, § 1.6(47), § 6.5.1(502)
 - synchrotron radiation, § 1.6(47), § 6.5.1(502)
- T**
- tandem, § 3.11.1(388)
 - tandem accelerator, § 1.11(98)
 - tapping, § 8.2(634)
 - tapping mode, § 7.3.1(560)
 - TCE, § 8.4(650)
 - technique, § 1.1(3)
 - Teller, § 2.7(185), § 7.5(608)
 - tellurium, § 7.4.3(588), § 7.4.4(599)
 - TEM, § 1.9(84), § 2.5.2(160), § 3.6.2(317), § 5.2(429), § 7.2.1(542), § 7.2.2(550), § 7.2.3(552), § 7.6(619), § 8.3(639)
 - temperature, § 2.6(180), § 2.7(185), § 6.8(526), § 8.4(650)
 - temperature programmed desorption (TPD), § 4.3(413)
 - ternary, § 6.2(459)
 - test, § 9.1(661)
 - tetrafluoroborate, § 6.3.2(479)
 - tetragonal, § 6.1(441), § 6.2(459)
 - tetrahedral, § 6.1(441)
 - tfac, § 2.5.3(172)
 - TGA, § 2.5.1(154), § 2.5.2(160), § 2.5.3(172), § 2.6(180)
 - theory, § 1.1(3)
 - thermal, § 8.4(650)
 - thermogravimetric analysis, § 2.5.3(172)
 - thermotropic, § 6.8(526)
 - thin film, § 1.8.1(75), § 1.11(98), § 7.2.1(542)
 - thiol, § 7.3.1(560)
 - thiophene, § 7.3.1(560)
 - thorium, § 1.13(111)
 - threose, § 3.7.4(336)
 - time of flight, § 3.11.1(388)
 - tin, § 6.1(441)
 - tip, § 7.3.1(560), § 8.2(634)
 - titanium sublimation pump, § 4.3(413)
 - TOF, § 6.7(518)
 - TOF-MS, § 3.10(380)
 - toluene, § 3.4.1(288)
 - toxics, § 3.10(380)
 - TPD theory, § 4.3(413)
 - TPD-MS, § 4.3(413)
 - trace, § 1.3(24)
 - trans, § 3.3.2(275)
 - transition, § 1.9(84), § 1.10(90), § 2.6(180)
 - transmission, § 1.6(47), § 1.9(84), § 3.5.2(304), § 6.5.1(502), § 7.2.1(542), § 7.2.2(550)
 - transport, § 7.3.2(567)
 - triclinic, § 6.1(441)
 - triplet, § 3.7.1(321), § 3.7.3(329)
 - tryptophan, § 3.5.2(304)
 - tungsten, § 8.3(639)
 - turbomolecular pump, § 4.3(413)
 - turbulent, § 1.4(28)
 - two photon, § 7.1(535)
 - tyrosine, § 3.5.2(304)
- U**
- UHV, § 4.3(413)
 - ultra-high vacuum, § 4.3(413)
 - ultrafast, § 3.3.4(283)
 - ultraviolet, § 7.4.3(588)
 - unit cell, § 6.1(441)
 - uranium, § 1.13(111)
 - UV, § 1.7.1(58), § 6.6(509)
 - UV-vis, § 7.4.1(577), § 7.4.3(588)
 - UV-visible, § 3.4.1(288), § 3.5.1(295)
- V**
- vacancies, § 6.1(441)
 - Vacancy, § 3.6.3(318)
 - vacuum, § 1.9(84), § 2.5.3(172), § 2.7(185), § 7.3.1(560)
 - valance, § 3.6.3(318)
 - valence band, § 7.4.2(580), § 7.4.4(599)
 - van der Waal, § 8.2(634)
 - van der Waals, § 7.3.1(560)
 - vapor, § 1.7.1(58), § 1.7.2(60)
 - vapor pressure, § 2.5.3(172)
 - Vergard's law, § 6.1(441)
 - Vertical Scanning Interferometry, § 8.1(623)

- vibration, § 1.7.1(58), § 3.3.4(283)
- Vickers, § 1.7.1(58)
- vinyl, § 3.3.2(275)
- visible, § 7.4.3(588)
- voltage, § 2.8(196), § 7.3.2(567), § 8.4(650), § 9.1(661)
- voltmeter, § 9.1(661)
- volume, § 2.7(185)
- von Laue, § 6.3.1(470)
- VSI, § 8.1(623)
- W** wafer, § 6.2(459)
- water, § 1.1(3), § 1.3(24), § 2.2(123), § 3.4.1(288), § 4.2(408), § 6.6(509), § 8.4(650)
- Watson, § 2.6(180)
- wave, § 6.8(526)
- wavelength, § 3.4.1(288), § 7.4.3(588), § 7.4.4(599)
- WDS, § 1.10(90)
- weight, § 2.3(129)
- Williams, § 3.7.6(347)
- Winefordner, § 1.7.1(58)
- Wollan, § 6.4(492)
- WOx, § 2.5.2(160)
- Wurtzite, § 6.1(441), § 6.2(459)
- X** X-ray, § 1.6(47), § 1.8.1(75), § 1.8.2(80), § 1.9(84), § 1.10(90), § 3.9.1(365), § 6.3.1(470)
- X-ray absorption, § 6.5.1(502)
- X-ray absorption fine structure spectroscopy, § 1.6(47), § 6.5.1(502)
- X-ray absorption near edge structure, § 1.6(47), § 6.5.1(502)
- X-ray absorption spectroscopy, § 1.6(47), § 6.5.1(502)
- X-ray diffraction, § 1.12(106)
- X-rays, § 1.6(47)
- XAFS, § 1.6(47), § 6.5.1(502)
- XANES, § 1.6(47), § 6.5.1(502)
- XAS, § 1.6(47), § 6.5.1(502)
- xenon, § 1.7.3(61), § 3.5.2(304)
- XPS, § 1.8.1(75), § 1.8.2(80), § 1.9(84), § 1.11(98), § 3.9.1(365)
- XRD, § 2.5.2(160), § 6.3.1(470)
- Z** zero-order, § 2.5.3(172)
- zinc, § 2.7(185), § 6.1(441), § 7.4.2(580), § 7.4.3(588), § 7.4.4(599)
- zinc blende, § 6.1(441), § 6.2(459)

Attributions

Collection: *Physical Methods in Chemistry and Nano Science*

Edited by: Andrew R. Barron

URL: <http://cnx.org/content/col10699/1.14/>

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Physical Methods in Chemistry and Nano Science"

Used here as: "Introduction"

By: Andrew R. Barron

URL: <http://cnx.org/content/m23040/1.9/>

Page: 1

Copyright: Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Introduction to Atomic Absorption Spectroscopy"

By: Hannah Rutledge, Andrew R. Barron

URL: <http://cnx.org/content/m38330/1.1/>

Pages: 3-17

Copyright: Hannah Rutledge, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "ICP-AES Analysis of Nanoparticles"

By: Alvin Orbaek, Andrew R. Barron

URL: <http://cnx.org/content/m22058/1.18/>

Pages: 17-23

Copyright: Alvin Orbaek, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "ICP-MS for Trace Metal Analysis"

By: Meghan Jebb, Andrew R. Barron

URL: <http://cnx.org/content/m34666/1.1/>

Pages: 24-28

Copyright: Meghan Jebb, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Introduction to Combustion Analysis"

By: Laurie Cullum, Andrew R. Barron

URL: <http://cnx.org/content/m43578/1.1/>

Pages: 28-43

Copyright: Laurie Cullum, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Ion Selective Electrode"

By: Huilong Fei, Andrew R. Barron

URL: <http://cnx.org/content/m43567/1.1/>

Pages: 43-47

Copyright: Huilong Fei, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "A Practical Introduction to X-ray Absorption Spectroscopy"

By: Natalia Gonzalez Pech, Andrew R. Barron

URL: <http://cnx.org/content/m38333/1.1/>

Pages: 47-58

Copyright: Natalia Gonzalez Pech, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Cold Vapor Atomic Fluorescence Spectroscopy"

By: Danielle Michaud, Andrew R. Barron

URL: <http://cnx.org/content/m38339/1.1/>

Pages: 58-60

Copyright: Danielle Michaud, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Detecting Mercury using Gold Amalgamation and Cold Vapor Atomic Fluorescence Spectroscopy"

By: Danielle Michaud, Andrew R. Barron

URL: <http://cnx.org/content/m38307/1.1/>

Pages: 60-61

Copyright: Danielle Michaud, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "The Application of Fluorescence Spectroscopy in the Mercury Ion Detection"

By: Lei Li, Andrew R. Barron

URL: <http://cnx.org/content/m38321/1.1/>

Pages: 61-75

Copyright: Lei Li, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "XPS Analysis of Modified Surfaces"

By: Lauren Harrison, Andrew R. Barron

URL: <http://cnx.org/content/m34527/1.1/>

Pages: 75-80

Copyright: Lauren Harrison, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Using XPS to Analyze Metal Nanoparticles"

By: Lauren Harrison, Andrew R. Barron

URL: <http://cnx.org/content/m34526/1.1/>

Pages: 80-83

Copyright: Lauren Harrison, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Auger Electron Spectroscopy"

By: Amanda M. Goodman, Andrew R. Barron

URL: <http://cnx.org/content/m43546/1.1/>

Pages: 84-90

Copyright: Amanda M. Goodman, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "An Introduction to Energy Dispersive X-ray Spectroscopy"

By: Graham Piburn, Andrew R. Barron

URL: <http://cnx.org/content/m43555/1.1/>

Pages: 90-98

Copyright: Graham Piburn, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Rutherford Backscattering of Thin Films"

By: Avishek Saha, Andrew R. Barron

URL: <http://cnx.org/content/m22411/1.3/>

Pages: 98-106

Copyright: Avishek Saha, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "An Accuracy Assessment of the Refinement of Crystallographic Positional Metal Disorder in Molecular Solid Solutions"

By: Andrew R. Barron, Simon Bott

URL: <http://cnx.org/content/m26148/1.2/>

Pages: 106-111

Copyright: Andrew R. Barron, Simon Bott

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Principles of Gamma-ray Spectroscopy and Applications in Nuclear Forensics"

By: Brandon Cisneros, Andrew R. Barron

URL: <http://cnx.org/content/m38345/1.1/>

Pages: 111-116

Copyright: Brandon Cisneros, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Melting Point Analysis"

By: Shawdon Molavi, Andrew R. Barron

URL: <http://cnx.org/content/m43565/1.1/>

Pages: 119-123

Copyright: Shawdon Molavi, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Solution Molecular Weight of Small Molecules"

By: Tawana Robinson, Andrew R. Barron

URL: <http://cnx.org/content/m43553/1.1/>

Pages: 123-129

Copyright: Tawana Robinson, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Molecular Weight of Polymers"

By: Sehmus Ozden, Andrew R. Barron

URL: <http://cnx.org/content/m43550/1.1/>

Pages: 129-144

Copyright: Sehmus Ozden, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Size Exclusion Chromatography and its Application in Polymer Science"

By: Yen-Hao Lin, Andrew R. Barron

URL: <http://cnx.org/content/m34657/1.2/>

Pages: 144-154

Copyright: Yen-Hao Lin, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Thermogravimetric Analysis of Single Walled Carbon Nanotubes"

By: Caoimhe de Fréin, Andrew R. Barron

URL: <http://cnx.org/content/m22972/1.2/>

Pages: 154-160

Copyright: Caoimhe de Fréin, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "TGA/DSC-FTIR Characterization of Oxide Nanaoparticles"

By: Nikolaos Soultanidis, Andrew R. Barron

URL: <http://cnx.org/content/m23038/1.2/>

Pages: 160-172

Copyright: Nikolaos Soultanidis, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Determination of Sublimation Enthalpy and Vapor Pressure for Inorganic and Metal-Organic Compounds by Thermogravimetric Analysis"

By: Andrew R. Barron

URL: <http://cnx.org/content/m33649/1.2/>

Pages: 172-180

Copyright: Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Differential Scanning Calorimetry (DSC)"

By: Basil Shadfan, Andrew R. Barron

URL: <http://cnx.org/content/m43548/1.1/>

Pages: 180-184

Copyright: Basil Shadfan, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "BET Surface Area Analysis of Nanoparticles"

By: Nina Hwang, Andrew R. Barron

URL: <http://cnx.org/content/m38278/1.1/>

Pages: 185-195

Copyright: Nina Hwang

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Introduction to Cyclic Voltammetry Measurements"

By: Xianyu Li, Andrew R. Barron

URL: <http://cnx.org/content/m34669/1.1/>

Pages: 196-205

Copyright: Xianyu Li, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Determination of Relaxation Parameters of Contrast Agents"

By: Ayrat Gizzatov, Andrew R. Barron

URL: <http://cnx.org/content/m38342/1.1/>

Pages: 206-210

Copyright: Ayrat Gizzatov, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Magnetics"

By: Samuel Maguire-Boyle, Andrew R. Barron

URL: <http://cnx.org/content/m22749/1.4/>

Pages: 213-225

Copyright: Samuel Maguire-Boyle, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Theory of A Superconducting Quantum Interference Device (SQUID)"

By: Samuel Maguire-Boyle, Andrew R. Barron

URL: <http://cnx.org/content/m22750/1.3/>

Pages: 225-234

Copyright: Samuel Maguire-Boyle, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Practical Guide to Using a Superconducting Quantum Interference Device"

By: Samuel Maguire-Boyle, Andrew R. Barron

URL: <http://cnx.org/content/m22968/1.2/>

Pages: 234-241

Copyright: Samuel Maguire-Boyle, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Raman and Surface-Enhanced Raman Spectroscopy"

By: Courtney Payne, Andrew R. Barron

URL: <http://cnx.org/content/m34528/1.1/>

Pages: 241-245

Copyright: Courtney Payne, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Characterization of Single-Walled Carbon Nanotubes by Raman Spectroscopy"

By: Richa Sethi, Andrew R. Barron

URL: <http://cnx.org/content/m22925/1.2/>

Pages: 245-259

Copyright: Richa Sethi, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Surface-Enhanced Raman Spectroscopy for the Study of Surface Chemistry"

By: Courtney Payne, Andrew R. Barron

URL: <http://cnx.org/content/m34522/1.1/>

Pages: 259-261

Copyright: Courtney Payne, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "IR Sample Preparation: A Practical Guide"

By: Paul Derry, Andrew R. Barron

URL: <http://cnx.org/content/m43564/1.1/>

Pages: 261-275

Copyright: Paul Derry, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Characteristic IR Vibrational Modes for Hydrocarbon Compounds"

By: Andrew R. Barron

URL: <http://cnx.org/content/m34623/1.1/>

Pages: 275-276

Copyright: Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Fourier Transform Infrared Spectroscopy of Metal Ligand Complexes"

By: Jiebo Li, Andrew R. Barron

URL: <http://cnx.org/content/m34660/1.1/>

Pages: 276-283

Copyright: Jiebo Li, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Pump-probe Detection of Molecular Functional Group Vibrational Lifetime"

By: Xiewen Wen, Andrew R. Barron

URL: <http://cnx.org/content/m34610/1.2/>

Pages: 283-288

Copyright: Xiewen Wen, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Basics of UV-Visible Spectroscopy"

By: Brittany L. Oliva, Andrew R. Barron

URL: <http://cnx.org/content/m34525/1.1/>

Pages: 288-294

Copyright: Brittany L. Oliva, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Photoluminescence Spectroscopy and its Applications"

By: Ruquan Ye, Andrew R. Barron

URL: <http://cnx.org/content/m38357/1.2/>

Pages: 295-304

Copyright: Ruquan Ye, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Fluorescence Characterization and its Application in DNA Detection"

By: Kewei Huang, Andrew R. Barron

URL: <http://cnx.org/content/m34680/1.1/>

Pages: 304-314

Copyright: Kewei Huang, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Introduction to Mossbauer Spectroscopy"

By: Ezekial Fisher, Andrew R. Barron

URL: <http://cnx.org/content/m22328/1.7/>

Pages: 315-317

Copyright: Ezekial Fisher, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Synthesis of Magnetite Nanoparticles"

By: Ezekial Fisher, Andrew R. Barron

URL: <http://cnx.org/content/m22167/1.6/>

Pages: 317-318

Copyright: Ezekial Fisher, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Mossbauer Analysis of Iron Oxide Nanoparticles"

By: Ezekial Fisher, Andrew R. Barron

URL: <http://cnx.org/content/m22619/1.3/>

Pages: 318-320

Copyright: Ezekial Fisher, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Determining the Chemical Formula of Nonstoichiometric Iron Oxide Nanoparticles by Mossbauer Spectroscopy"

By: Ezekial Fisher, Andrew R. Barron

URL: <http://cnx.org/content/m22184/1.4/>

Pages: 320-321

Copyright: Ezekial Fisher, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Introduction to Nuclear Magnetic Resonance Spectroscopy"

By: Ty Hanna, Andrew R. Barron

URL: <http://cnx.org/content/m38356/1.1/>

Pages: 321-326

Copyright: Ty Hanna, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "NMR Properties of the Elements"

By: Andrew R. Barron

URL: <http://cnx.org/content/m34632/1.1/>

Pages: 326-329

Copyright: Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "NMR Spin Coupling"

By: Jarrod Boyd, Andrew R. Barron

URL: <http://cnx.org/content/m43551/1.1/>

Pages: 329-336

Copyright: Jarrod Boyd, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "NMR Spectroscopy of Stereoisomers"

By: Sequoyah King, Andrew R. Barron

URL: <http://cnx.org/content/m38355/1.1/>

Pages: 336-340

Copyright: Sequoyah King

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Basics of Solid-State NMR"

By: Gabriel Oaxaca, Andrew R. Barron

URL: <http://cnx.org/content/m43547/1.1/>

Pages: 340-347

Copyright: Gabriel Oaxaca, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Lanthanide Shift Reagents"

By: Mayra Hernandez Rivera, Andrew R. Barron

URL: <http://cnx.org/content/m43580/1.1/>

Pages: 347-355

Copyright: Mayra Hernandez Rivera, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "EPR Spectroscopy: An Overview"

By: Cara Bovet, Andrew R. Barron

URL: <http://cnx.org/content/m22370/1.3/>

Pages: 355-359

Copyright: Cara Bovet, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Electron Paramagnetic Resonance Spectroscopy of Copper(II) Compounds"

By: Cara Bovet, Andrew R. Barron

URL: <http://cnx.org/content/m22507/1.2/>

Pages: 359-364

Copyright: Cara Bovet, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "XPS of Carbon Nanomaterials"

By: Ariana Bratt, Andrew R. Barron

URL: <http://cnx.org/content/m34549/1.2/>

Pages: 365-380

Copyright: Ariana Bratt, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "ESI-QTOF-MS Coupled to HPLC and its Application for Food Safety"

By: Gedeng Ruan, Andrew R. Barron

URL: <http://cnx.org/content/m38334/1.1/>

Pages: 380-387

Copyright: Gedeng Ruan, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Principles of Mass Spectrometry and Modern Applications"

By: Justin Law, Andrew R. Barron

URL: <http://cnx.org/content/m38353/1.1/>

Pages: 388-394

Copyright: Justin Law, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Dynamic Headspace Gas Chromatography Analysis"

By: Zhun Zhao, Andrew R. Barron

URL: <http://cnx.org/content/m34622/1.1/>

Pages: 397-408

Copyright: Zhun Zhao

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Gas Chromatography Analysis of the Hydrodechlorination Reaction of Perchloroethylene"

By: Zhun Zhao, Andrew R. Barron

URL: <http://cnx.org/content/m34634/1.1/>

Pages: 408-413

Copyright: Zhun Zhao

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Temperature-Programmed Desorption Mass Spectroscopy Applied in Surface Chemistry"

By: Chih-Chau Hwang, Andrew R. Barron

URL: <http://cnx.org/content/m38319/1.1/>

Pages: 413-423

Copyright: Chih-Chau Hwang, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "NMR of Dynamic Systems: An Overview"

By: Chengmin Jiang, Andrew R. Barron

URL: <http://cnx.org/content/m43679/1.1/>

Pages: 425-429

Copyright: Chengmin Jiang, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Rolling Molecules on Surfaces Under STM Imaging"

By: Pinn-Tsong Chiang, Andrew R. Barron

URL: <http://cnx.org/content/m22965/1.3/>

Pages: 429-439

Copyright: Pinn-Tsong Chiang, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Crystal Structure"

By: Andrew R. Barron, Carissa Smith

URL: <http://cnx.org/content/m16927/1.10/>

Pages: 441-458

Copyright: Andrew R. Barron, Carissa Smith

License: <http://creativecommons.org/licenses/by/2.0/>

Module: "Structures of Element and Compound Semiconductors"

By: Andrew R. Barron

URL: <http://cnx.org/content/m23905/1.6/>

Pages: 459-470

Copyright: Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "An Introduction to X-ray Diffraction"

By: Wayne Lin, Andrew R. Barron

URL: <http://cnx.org/content/m38289/1.1/>

Pages: 470-479

Copyright: Wayne Lin, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Refinement of Crystallographic Disorder in the Tetrafluoroborate Anion"

By: John J. Allen, Andrew R. Barron

URL: <http://cnx.org/content/m36687/1.3/>

Pages: 479-491

Copyright: John J. Allen, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Neutron Diffraction"

By: Gabriela Escalera, Andrew R. Barron

URL: <http://cnx.org/content/m43582/1.1/>

Pages: 492-502

Copyright: Gabriela Escalera, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "XAFS Analysis for Arsenic Adsorption onto Iron Oxides"

By: Natalia Gonzalez Pech, Andrew R. Barron

URL: <http://cnx.org/content/m38287/1.2/>

Pages: 502-509

Copyright: Natalia Gonzalez Pech, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Circular Dichroism Spectroscopy and its Application for Determination of Secondary Structure of Optically Active Species"

By: Farrukh Vohidov, Andrew R. Barron

URL: <http://cnx.org/content/m38277/1.2/>

Pages: 509-517

Copyright: Farrukh Vohidov, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Protein Analysis using Electrospray Ionization Mass Spectroscopy"

By: Wilhelm Kienast, Andrew R. Barron

URL: <http://cnx.org/content/m38341/1.1/>

Pages: 518-525

Copyright: Wilhelm Kienast, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "The Analysis of Liquid Crystal Phases using Polarized Optical Microscopy"

By: Changsheng Xiang, Andrew R. Barron

URL: <http://cnx.org/content/m38343/1.2/>

Pages: 526-533

Copyright: Changsheng Xiang, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Microparticle Characterization via Confocal Microscopy"

By: Charles Conn, Andrew R. Barron

URL: <http://cnx.org/content/m34540/1.1/>

Pages: 535-542

Copyright: Charles Conn, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Transmission Electron Microscopy"

Used here as: "Transmission Electron Microscopy: An Overview"

By: Yen-Tien Lu, Andrew R. Barron

URL: <http://cnx.org/content/m34523/1.1/>

Pages: 542-550

Copyright: Yen-Tien Lu, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Transmission Electron Microscopy Image for Multilayer-Nanomaterials"

By: Yen-Tien Lu, Andrew R. Barron

URL: <http://cnx.org/content/m34524/1.1/>

Pages: 550-552

Copyright: Yen-Tien Lu, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "TEM Imaging of Carbon Nanomaterials"

By: Zhengzong Sun, Andrew R. Barron

URL: <http://cnx.org/content/m22963/1.5/>

Pages: 552-559

Copyright: Zhengzong Sun, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/2.0/>

Module: "Scanning Tunneling Microscopy of Nanomaterials"

By: Zhiwei Peng, Andrew R. Barron

URL: <http://cnx.org/content/m38335/1.2/>

Pages: 560-567

Copyright: Zhiwei Peng, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Adaptations to Scanning Tunneling Microscopy"

By: Michelle LaComb, Andrew R. Barron

URL: <http://cnx.org/content/m43549/1.1/>

Pages: 567-577

Copyright: Michelle LaComb, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Using UV-vis for the detection and characterization of silicon quantum dots"

By: Brittany L. Oliva, Andrew R. Barron

URL: <http://cnx.org/content/m34655/1.1/>

Pages: 577-580

Copyright: Brittany L. Oliva, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Optical Properties of Group 12-16 (II-VI) Semiconductor Nanoparticles"

By: Sravani Gullapalli, Andrew R. Barron

URL: <http://cnx.org/content/m34553/1.1/>

Pages: 580-588

Copyright: Sravani Gullapalli

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Characterization of Group 12-16 (II-VI) Semiconductor Nanoparticles by UV-visible Spectroscopy"

By: Sravani Gullapalli, Andrew R. Barron

URL: <http://cnx.org/content/m34601/1.1/>

Pages: 588-599

Copyright: Sravani Gullapalli

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Optical Characterization of Group 12-16 (II-VI) Semiconductor Nanoparticles by Fluorescence Spectroscopy"

By: Sravani Gullapalli, Andrew R. Barron

URL: <http://cnx.org/content/m34656/1.1/>

Pages: 599-608

Copyright: Sravani Gullapalli

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Measuring the Specific Surface Area of Nanoparticle Suspensions using NMR"

By: Varun Shenoy Gangoli, Andrew R. Barron

URL: <http://cnx.org/content/m34663/1.1/>

Pages: 608-618

Copyright: Varun Shenoy Gangoli

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Characterization of Graphene by Raman Spectroscopy"

By: Zheng Yan, Andrew R. Barron

URL: <http://cnx.org/content/m34667/1.2/>

Pages: 619-622

Copyright: Zheng Yan, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "The Application of VSI (Vertical Scanning Interferometry) to the Study of Crystal Surface Processes"

By: Inna Kurganskaya, Andreas Luttgé, Andrew R. Barron

URL: <http://cnx.org/content/m22326/1.4/>

Pages: 623-634

Copyright: Inna Kurganskaya, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Atomic Force Microscopy"

By: Ryan Thaner, Andrew R. Barron

URL: <http://cnx.org/content/m34664/1.1/>

Pages: 634-639

Copyright: Ryan Thaner, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "SEM and its Applications for Polymer Science"

By: Stacy Prukop, Andrew R. Barron

URL: <http://cnx.org/content/m38344/1.1/>

Pages: 639-649

Copyright: Stacy Prukop, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "Catalyst Characterization Using Thermal Conductivity Detector"

By: Juan Velazquez, Andrew R. Barron

URL: <http://cnx.org/content/m43579/1.1/>

Pages: 650-659

Copyright: Juan Velazquez, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Module: "A Simple Test Apparatus to Verify the Photoresponse of Experimental Photovoltaic Materials and Prototype Solar Cells"

By: Dennis J. Flood, Andrew R. Barron

URL: <http://cnx.org/content/m42271/1.1/>

Pages: 661-669

Copyright: Dennis J. Flood, Andrew R. Barron

License: <http://creativecommons.org/licenses/by/3.0/>

Physical Methods in Chemistry and Nano Science

Chem 475 at Rice University is a survey course of research techniques used in modern chemistry and nano-materials science.

About Connexions

Since 1999, Connexions has been pioneering a global system where anyone can create course materials and make them fully accessible and easily reusable free of charge. We are a Web-based authoring, teaching and learning environment open to anyone interested in education, including students, teachers, professors and lifelong learners. We connect ideas and facilitate educational communities.

Connexions's modular, interactive courses are in use worldwide by universities, community colleges, K-12 schools, distance learners, and lifelong learners. Connexions materials are in many languages, including English, Spanish, Chinese, Japanese, Italian, Vietnamese, French, Portuguese, and Thai. Connexions is part of an exciting new information distribution system that allows for **Print on Demand Books**. Connexions has partnered with innovative on-demand publisher QOOP to accelerate the delivery of printed course materials and textbooks into classrooms worldwide at lower prices than traditional academic publishers.